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DEPARTMENT OF ENVIRONMENT
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PACIFIC AND YUKON REGION

# PROCEEDINGS OF
# PULP MILL EFFLUENT MONITORING:

An Information Development Program
Sponsored by the Environmental Protection Service -
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Regional Program Report: 83-15

Edited by

W.M. Pomeroy

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## ABSTRACT

An apparent lack of understanding and agreement exists in many cases between industry, their consultants, government regulatory agencies and the research community as to the seriousness of environmental impacts associated with the discharge of pulp mill effluent to coastal marine waters. This has led to problems in the formulation of and agreement on monitoring programs. As a first step towards resolving this situation, the Environmental Protection Service decided to sponsor a two day program designed to promote information exchange and the development of common concerns.

Investigators working in the areas of physical, chemical and biological effects of pulp mill effluent were invited to present the results of their studies during the first day and a half. These formed the basis for discussions centering on data gaps, research needs, priorities, and current extent of environmental impact scheduled for the last day of the program. This report contains the papers presented, or an abstract in the case where the paper is being submitted for publication in a primary scientific journal.

## RÉSUMÉ

En de nombreuses occasions, un manque de compréhension et de consensus s'est fait sentir entre l'industrie, ses conseillers, les organismes gouvernementaux de réglementation et les chercheurs sur le degré de gravité des effets produits sur l'environnement par le déversement dans les eaux du littoral des effluents rejetés par les usines de pâte à papier. Ce manque de consensus a rendu difficile la formulation des programmes de contrôle de la pollution et l'accord des différentes parties sur ces programmes. Comme première mesure destinée à résoudre ce problème, le Service de la protection de l'environnement a décidé de parrainer deux journées d'études destinées à promouvoir les échanges d'information et à préciser les préoccupations communes.

Les enquêteurs travaillant dans les domaines des effets physiques, chimiques et biologiques des effluents rejetés par les usines de pâte à papier ont été invités à présenter durant la première journée et demie les résultats de leurs recherches. Leurs rapports ont fourni une base de discussions pour le dernier jour de la réunion, discussions axées sur les lacunes dans les données, les basoins de la recherche, les priorités et le degré de gravité actuel des effets sur l'environnement. Le rapport dont ceci est le résumé contient les mémoires présentés ou simplement un résumé des mémoires lorsque deux-ci étaient destinés à être publies dans des revues scientifiques.

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Keynote Address

# WATER POLLUTION FROM PULPMILL EFFLUENT IN BRITISH COLUMBIA:

# A GENERAL OVERVIEW.

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## ABSTRACT

The pulp and paper industry of British Columbia experienced its greatest growth during the 1950s and 60s. There were 10 mills on the coast and in the interior in 1961, and this had increased to 12 mills on the coast, and 9 mills in the interior (not considering the 4 small paper mills in the New Westminster area) by 1975. By 1983 one of the coastal mills (Ocean Falls) had been completely closed down. The industry is at a low ebb at the present time, because of the economic recession. Water pollution from the industry is no more acute now, and may be less so, than it was in 1970. It is anticipated, however, that the industry will rebound in the next decade and new pollution problems will arise in both coastal and interior waters as production increases, with possibly new and expanded installations throughout the province. The trends of the last two decades will probably continue with installation of mainly kraft and newsprint mills predominantly at interior locations.

The most acute water pollution has been associated with sulphite pulp mills on the coast. All 5 sulphite mills eventually converted to kraft production, except for one (Port Alice), which converted from a calcium bisulphite base to a recoverable ammonia bisulphite base. Interior mills nearly all have settling ponds for recovery of wood solids, biobasins for reduction of BOD (biochemical oxygen demand) and toxicity, and they discharge effluent through diffusers at midstream in rivers for rapid dilution and dispersion. Coastal mills usually have clarifiers or settling basins for removal of wood solids, and diffusers on submarine outfalls for effective dilution and dispersion.

Low dissolved oxygen concentrations have been the major pollution problems encountered in receiving waters for effluent from sulphite mills (i.e., Neroutsos Inlet, adjacent to Port Alice and Wainwright Basin - Porpoise Harbour, adjacent to Prince Rupert). Low oxygen conditions have also arisen in Alberni Harbour, mainly from effluent BOD, but also from wood solids decomposing in the sediment. The colour of the effluent inhibits light penetration and retards photosynthesis and the associated oxygen release. No acute toxicity of pulpmill effluent to aquatic life has been recorded but sublethal stresses on juvenile and adult salmon may have occurred in both freshwater and marine environments. There is a need for research on such sublethal effects of pulpmill effluents as disruption of migration behaviour and impairment of swimming performance in adult salmonids, interference with feeding and reduction in growth of fish and invertebrates, and the disturbance of the predator-prey relationship. Impairment of swimming performance of adult sockeye, for example, migrating to distant spawning grounds in the Fraser River system, e.g., Stuart Lake, could affect reproduction in that some of the fish could die unspawned, and thereby affect stocks.

A need exists for research on methods to minimize losses of product (fibre) and process chemicals in pulp and paper mills, which would not only reduce pollution but could increase industry profits. Research is also needed on improved techniques for removal of wood solids from effluents and reduction of their BOD and toxicity, particularly toxicity of the more refractory components such as resin acids and organochlorines. Operation of settling ponds and biobasins is still carried out largely as an art, based on the skill, experience and judgement of the operator, rather than as a science based on established control parameters for most efficient operation. Some of the operators' information on treatment reaches the technical literature, but it would be valuable to have data on the variation in treatment performance under different controlled conditions carefully documented. No doubt, this type of information would be useful to the industry, especially for new mills designing and starting up their treatment systems, and there would be overall benefits for water pollution control.

## 1. INTRODUCTION

When I was asked by your convenor several weeks ago to give the introductory talk in this Symposium, I had an initial impulse to graciously decline, because it has been some years since I worked directly on problems of pulpmill pollution. On a quick second thought, however, it occurred to me that this might be an opportunity for me to learn something about current research in the field, so I agreed. Before I had the chance to change my mind, Dr. Pomeroy was back to me asking for a title to my talk. I hastily gave him a tentative title off the top of my head, which was as general as possible. It is listed in part as "A General Overview". I think now that it would have been better stated as "A Historical Perspective". My thoughts will be put forward essentially in that context.

I would like to remark initially that this might be regarded as an unusual time to hold a Symposium on the problems of pulpmill pollution. Usually these kinds of gatherings are held at a time when the economy is booming, industry is operating at full swing, new developments are underway and established plants are undergoing expansion. Nothing could be farther from this state of affairs in the pulp and paper industry of British Columbia at the present time. In talking with one forest industry executive at the end of 1982, I learned that there was not a pulp and paper mill in the province that was not losing money. Some were losing more than others. Markets were down and not expected to improve for some time. The biggest decisions that pulp and paper mill management had to make was to determine when a particular mill had to be closed and for how long. There is a cost associated with keeping a mill closed. By some formula, management calculates at what stage a mill loses less money by closing down than by continuing operation.

So what rationale is there for a Symposium like this in these rather bleak economic times? I would say that it may be a good time to take stock and see what we know at present about problems of pulpmill pollution and look a little bit into the future to get some idea of what problems remain unsolved and what new problems may be looming on the horizon. There is little question in my mind that the pulp and paper industry will eventually experience an upswing in demand for its products on both the domestic and international markets. Numerous factors that only economists understand will determine how soon this will be. One thing that is certain is that utilization of pulp and paper products never declines significantly in our society. People will always continue to read newspapers and newspapers seem to become thicker by the year. When the inevitable increase in demand for these products occurs, we will probably find once again an under-capacity in British Columbia's pulp and paper industry.

Historically, we saw an increase in the number of pulp and paper mills, mainly on the coast, in the early post-war years (1948-1956); then there was a period of expansion of existing mills (1956-1960); and this was followed by a series of new pulp mills in the interior of the province (1960-1970). The decade 1970-1980 was essentially one of stabilization, with some over-capacity at first and then high productivity with good markets at the end of the 70's decade and early 80's, fostered by Canada's favourable position in world markets due to the decline in the value of the Canadian dollar. The big slump occurred in 1982. I would predict that by the middle of the present decade there will be a marked rise in demand for Canadian pulp and paper products and the existing mills will not be able to cope with the demand. There will be expansion of existing mills and replacement of worn-out and outdated facilities. Plans for new mills that were developed in the 1960's will be dusted off and revived, and perhaps even some new plans may emerge.

The time to begin thinking environmentally about this upcoming onslaught of pulp and paper mill activity is now. What are the new developments in processes in the industry? Do the new processes lead to production of hazardous substances that end up in the effluent discharged into our streams and coastal waters? What effects would they have on our living aquatic resources? Are these substances amenable to treatment? Are there better alternative ways for treating pulp and paper mill effluent from those being used at present? Is a closed system with

recycling (e.g., Rapson process) practical? What about the locations of pulp and paper mills from the environmental and aquatic habitat point of view? Have we learned some lessons from the past? Could industry be persuaded to reveal their plans to the regulatory agencies early in their deliberations before they become locked into real estate deals and other arrangements that lead to an inflexible situation? What kinds of options exist for properly locating mills on rivers and on the coast to minimize the effects of effluent discharge?

I would like to highlight in this paper the kinds of problems in disposal of pulp and paper mill effluents that I visualize as being the most significant from the point of view of aquatic environmental quality and fisheries habitats. In so doing, I will touch on certain problems that have arisen in the past and how we managed to deal with them. I should say that during the period of much activity in the pulp and paper industry of British Columbia, from 1950 to 1970, a comparatively small group in the Department of Fisheries and the Fisheries Research Board handled the pulp and paper mill problems. We met regularly with industry on specific pulp and paper mill issues and managed to achieve good control of pollution, often based on rather scanty basic knowledge, at most of the new mills and in areas where expansions of existing mills were occurring during that 20-year period. I should add that we had much valuable collaboration from staff of the International Pacific Salmon Fisheries Commission's Sweltzer Creek Laboratory during the period of construction of new mills on the Fraser River system in the 60's. That collaboration has continued to the present time on problems of waste disposal from pulp and paper mills, as well as on those of other pollution sources , e.g. sewage, in the Fraser River.

## 2. DISTRIBUTION OF PULP MILLS IN BRITISH COLUMBIA AND POTENTIAL IMPACT ON LIVING RESOURCES

When I first started employment with the Fisheries Research Board thirty years ago, there were 8 major pulp mills in Britsh Columbia and all of them were on the coast. By 1961 there were 10 mills on the coast and one in the interior at Castlegar on the Columbia River (Fig. 1). Now there are some two dozen mills in the province and half of them are in the interior (Fig. 2).

A general trend during the last three decades has been to move from the coast

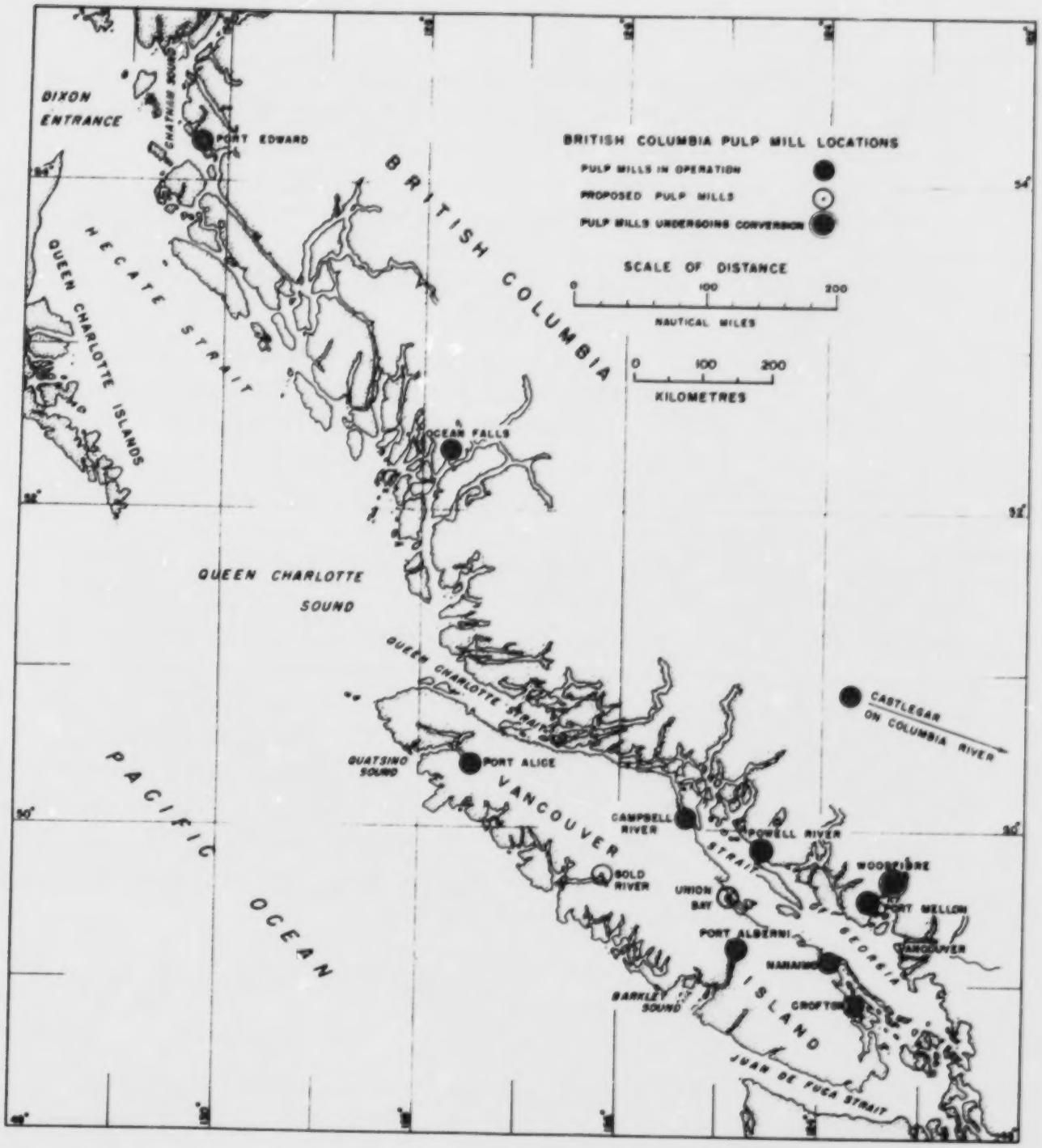


Figure 1. Locations of pulp mills in British Columbia in 1961.

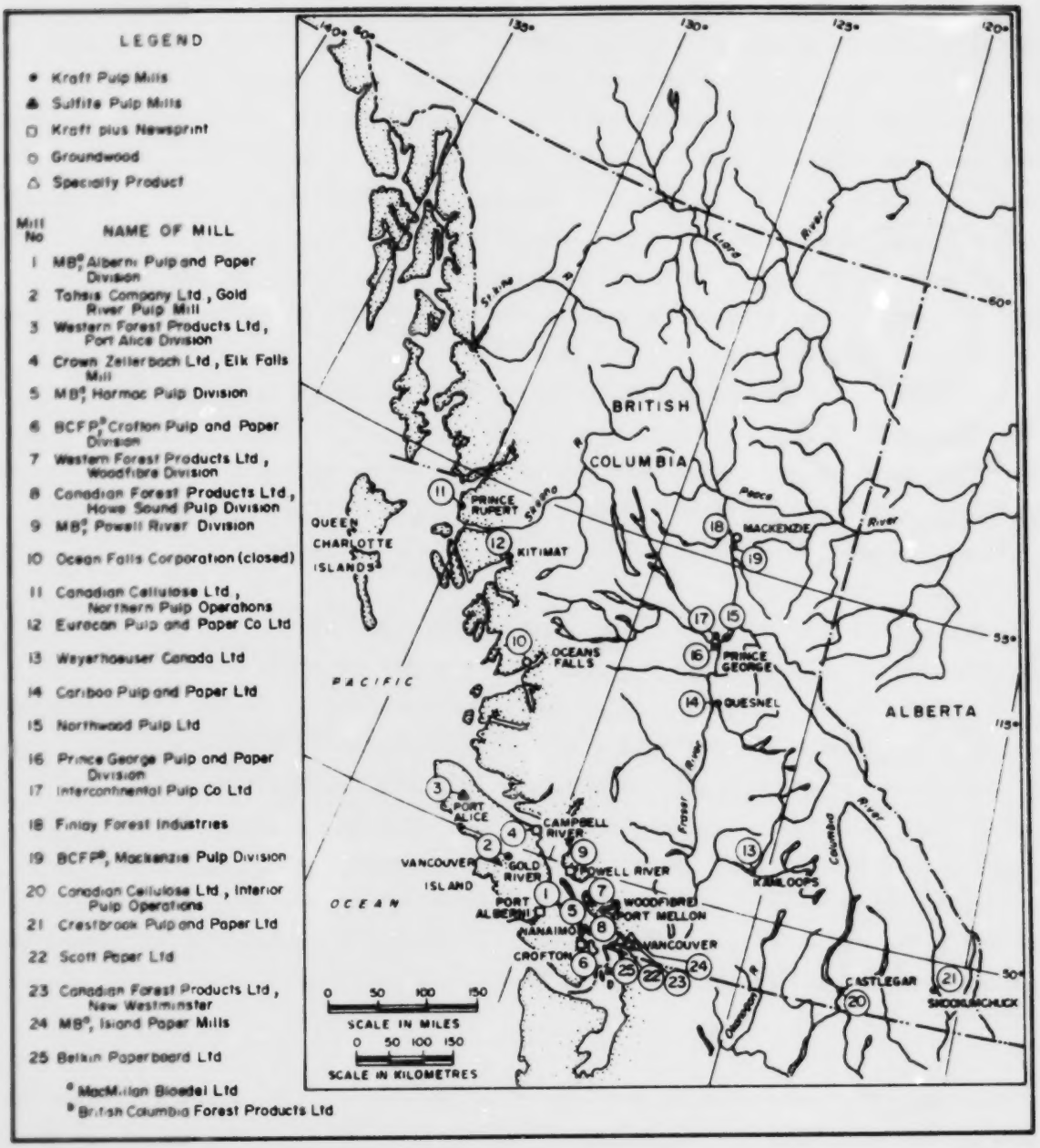


Figure 2. Locations of pulp mills in British Columbia in 1983.

to the interior in siting pulp mills. After the Castlegar pulp mill was installed, we had a pulp mill constructed at Kamloops and then a rash of pulp mills at Prince George. We were not too concerned about the pulp mill at Castlegar, because it did not threaten our salmon resources, although it could have had some effect on the freshwater species of the upper Columbia and possibly on salmonids in the U.S. section of lower Columbia. But the mills at Kamloops and Prince George, and later at Quesnel, could definitely have a potential impact on the important salmon runs in the Fraser and Thompson rivers. We spent a great deal of time in reviewing the proposals for constructing mills on these rivers and for effluent treatment facilities. Other interior mills, such as the ones at Skookumchuck on the Kootenay River draining into the Columbia River system, and at Mackenzie on Williston Lake, draining to the north and ultimately into the Peace River system, have not caused much concern from the salmon point of view. We have generally left these mills to the provincial Fish and Wildlife Branch to worry about with respect to protecting the freshwater sport species.

During the period of the 1950s and 60s when there was much planning for and construction of pulp mills in the province, a number of other coastal sites were actively considered. These included Union Bay near Courtenay, Squamish, a second pulp mill at Nanaimo and two pulp mills proposed in the late 60s for Bella Coola. Of course, in the end, even if markets are available for additional pulp and paper, there must be an adequate wood supply to meet any additional production schedule. We appear to be close to saturation in the province as far as utilization of available wood supplies is concerned, on a sustained-yield basis. Any new mills may have to be replacements for old mills, which will be phased out, and their wood supplies through tree harvesting permits made available to the new mills.

In general, coastal mills are less of a threat to living resources than the interior mills. There are exceptions, however, and certain existing and proposed coastal mills could have a serious impact on not only salmonids but also on such other commercially valuable species as oysters. Companies seem to have a penchant for siting mills in areas where living resources and the multiple use of waters inevitably leads to conflicts. The proposed mill at Union Bay, if it had gone ahead, could have had disastrous effects on the important oyster industry in Baynes Sound. Mill sites are often chosen at or near estuaries, and needless to

say, mills at such locations can be a serious threat to salmonids, both juveniles migrating downstream and adults bound for the spawning grounds. Moreover, the food supply of the juveniles can be seriously affected on the estuarine nursery grounds. In the early days, we actually did not pay too much attention to this possible adverse effect, although we know now that it could be more important than the effect on the fish themselves.

## 3. TYPES OF MILLS

There are basically three types of processes in wood pulp production in British Columbia, and this is probably true for pulp mills anywhere in the world. These are the two major chemical pulping processes, kraft and sulphite, and the mechanical pulping process that produces groundwood by mechanically grinding the wood. There are numerous variations of the latter process. A form of bleaching or brightening of the pulp is usually carried out following each pulp-forming process.

If one could identify a consistent trend in the pulp and paper industry during the last half century, besides the growth in the number of mills, it would have to be the tendency to build kraft pulp mills instead of sulphite pulp mills and to convert the few sulphite mills we have had in the province to kraft production. In 1950, there were five mills in the province producing sulphite pulp, located at Prince Rupert, Ocean Falls, Port Alice, Powell River and Woodfibre. Some of these were small producers of sulphite to provide long-fibred pulp to strengthen newsprint, which is made mostly from short groundwood fibres. We now have only one sulphite producer. The sulphite mill at Port Alice is one of the oldest mills in the province, dating back to 1917. It has been one of the more serious polluters in the province and has recently undergone modernization with some major conversions. The trend toward kraft pulp is not so much due to less water pollution from the kraft process than the fact that there has apparently been a greater demand for the kraft product.

### 3.1 Sulphate or Kraft Pulp

Traditionally known as sulphate pulp, because of the use of sodium sulphate in the cooking process, "kraft" is now the more commonly used term, having

originated from the German word for "strong", implying a strong fibre. The kraft process is also sometimes referred to as the alkaline chemical process, because caustic (sodium hydroxide) is used in the digestion of the wood chips. In addition, sodium sulphide is an important ingredient of the cooking liquor, the concentration of which is termed as the "sulphidity" in the trade. The sulphide, of course, gives the kraft process the typically unpleasant odour. Wood chips prepared in the chipper from bark-free logs are immersed in the "white liquor", consisting of the various sodium salts and caustic in measured proportions, and cooked for several hours at elevated temperature and pressure. This separates the lignin, hemi-celluloses, sugars and other soluble organic constituents from the insoluble fibre consisting of cellulose. The traditional technique of digestion was in a batch digester which was kept closed for several hours until the chips were fully cooked. Then the digester was "blown", which means that the pressure was released and the contents discharged to a large vat, where the "black liquor" could be drained from the fibres. Then the fibres were washed with water to remove any clinging black liquor. In more recent times, during the last 20 years, the batch digester has been largely replaced by the continuous digester. The Kamyr digester of Swedish design pioneered in this field. This meant that chips could be fed into the system continuously and fibre taken off in a steady stream at the other end, with subsequent draining, washing and drying or bleaching also taking place in a continuous process. This all lends itself more conveniently to an assembly-line type of operation than the batch process.

The kraft process has always had associated with it a recycling system, which is considered an important element in the economy of kraft pulp production. It is also extremely important from the pollution control point of view. The "black liquor" is evaporated and burned in the furnaces. A certain amount of energy is derived in this way, but more importantly, salts are recovered. The salt cake residue from combustion is dissolved in water or a caustic solution to produce "green liquor". This then becomes the base for the next batch of white liquor for digesting chips. The insoluble residues filtered out of the green liquor are discharged to waste as "green liquor dregs". They are comparatively inert. One of the characteristics they possess, which could be taken advantage of in mills, is effective anti-foaming properties (Waldichuk 1964b). Rather than applying expensive commercial anti-foaming agents to suppress foam in effluents, the green liquor dregs might be able to do the job equally as well.

The final effluent from a modern conventional unbleached kraft mill consists of pulp wash waters too dilute in black liquor to be recovered, although wash waters are now recycled in the washers until they become rich enough in black liquor for recovery. Evaporator condensates from the recovery room often go to the sewer, if there is not a scheme for mixing them with wash waters. Floor drainage, of course, proceeds directly to the sewer. The total effluent from an unbleached kraft mill is usually alkaline with a pH generally between 9 and 10.

Most kraft mills now have associated with them bleach plants to provide some degree of bleaching for the pulp. This may be a full-bleach operation with seven stages to provide a high degree of brightness for the pulp. Or it may be a so-called semi-bleach with only three stages of bleaching, yielding only a modest amount of brightening for newsprint application. In almost all cases, the first bleaching stage is caustic extraction, which dissolves out various coloured constituents clinging to the fibre. This is usually the effluent stream that gives total pulpmill effluent most of its brown colour. Following caustic extraction, there are various stages of treatment with chlorine, chlorine dioxide and sodium hypochlorite. The caustic extraction effluent is alkaline, while the chlorine-containing streams are acidic. We have often advocated that these streams be mixed prior to discharge, in order that some measure of neutralization be achieved. Company personnel frequently avoid mixing the two streams because foam is inevitably produced.

Much of the toxicity of bleached kraft pulp mills is due to bleach-plant effluent. In freshwater particularly, the effect of high or low pH may be important because of the low buffering capacity of freshwater. Chlorinated organic compounds in chlorination bleach effluents may present toxicity and bioaccumulation problems in both freshwater and seawater, but the importance of this is not yet too well established.

### 3.2 Sulphite Pulp

An acidic chemical process, the conventional production of sulphite pulp depends on digestion of wood chips at elevated temperature and pressure in a solution of calcium bisulphite. After digestion, the fibre is separated from the resulting cooking solution, which is referred to as "red liquor". Traditionally,

the red liquor is not processed for recovery of energy and salts, because of problems of scaling (calcium salts precipitate at higher temperatures), corrosion, and problematical re-use of salt-cake from the furnaces. The red liquor is usually discharged, therefore, to the nearest water course. It is rich in wood sugars, lignins and hemi-celluloses, which create many problems in the aquatic environment, particularly depletion of dissolved oxygen. It is estimated that for every ton of pulp produced by the sulphite process an equal amount of the soluble component of the wood plus the chemicals added in digestion enter the sewer.

Efforts have been made in the last 30 years to reduce the pollution potential of sulphite pulp mills. Red liquor from calcium-based sulphite mills has been used for by-products such as alcohol, adhesives, drilling muds, vanillin and assorted chemicals. But markets for any of these products can be rather quickly saturated by the production potential from available spent sulphite liquor.

A promising approach to reducing the water pollution caused by sulphite mills has been the introduction of a more soluble base for the cooking solution. Calcium has been replaced by magnesium, sodium or ammonia in the bisulphite cooking solution of some sulphite mills. These have all met with various problems, not the least of which has been a poorer quality of fibre product in some cases. Few sulphite mills with a non-calcium base have been fully amenable to the type of recovery that exists in virtually all kraft mills. Conversion to the ammonia base has been most common, but few mills have been able to put the system through the whole cycle of burning the effluent and recovering the salts. They only burn the evaporated spent liquor and end up with a large clinker in the furnace that must be disposed of. This appears to be the case with the sulphite pulp mill at Port Alice. Weyerhaueser at Springfield, Oregon, introduced the magnesium base for their sulphite mill and that appears to have been quite successful. I am uncertain, however, whether they have full recovery at that mill. Certainly the ecological impact of magnesium-base sulphite mills with recovery has been lessened compared to those sulphite mills without recovery (Limerick, 1973).

Different grades of sulphite pulp are produced, and the characteristics of the effluent discharged varies according to the grade. The dissolving sulphite for rayon-type fabrics once produced at the Columbia Cellulose mill in Prince

Rupert was a high quality sulphite grade. It contributed to a highly enriched red liquor with rather acute water-pollution potential.

The two mills that have caused the most serious pollution problems in the province were the two major sulphite mills, located at Port Alice (Waldichuk 1958) and Prince Rupert (Waldichuk 1966). Low dissolved oxygen concentrations in receiving waters have been the main concerns. Changes at these mills during the last two decades, with conversions from sulphite to kraft at the Prince Rupert mill and to a recoverable sulphite base at the Port Alice mill, have greatly ameliorated the water pollution problems.

During the course of conversion of the Port Alice mill, from a calcium base to ammonia base and installation of a submarine diffuser for disposal of effluent, several cooperative studies were conducted to determine the changes in environmental conditions in Neroutsos Inlet (Davis et al. 1978; Tollefson and Tokar 1978; Greer and Futer 1979). There are indications that good progress has been made in restoring the dissolved oxygen to more normal levels in the surface layer of Neroutsos Inlet.

### 3.3 Groundwood

Production of groundwood is vital for the newsprint business. It is often referred to as mechanical pulping. Wood is simply ground by some mechanical means to obtain fibres that can be formed into newsprint. They are usually short fibres. Longer fibres are added from chemical pulping to provide the needed strength.

The traditional technique for producing groundwood is by rubbing blocks of wood with abrasive rotating stone wheels. Water is added during the grinding process, and this forms a slurry of short-fibred pulp. There are other techniques now for producing mechanical pulp by cutting wood with sharp steel-knives to produce what is known as refiner-ground pulp. But in all cases, the wood is maintained at either room temperature or somewhat elevated owing to the heat from friction induced by grinding stones or cutting steel edges. There is some leaching of organic constituents from the wood through exposure to water of the more soluble components within the wood, but the components that are relatively insoluble in water at room temperature remain with the wood fibres.

A new technique is now available for producing groundwood at an elevated temperature. This is thermo-mechanical pulping, and it is being utilized for the first time in the province at a new groundwood mill at Quesnel. The pulp produced by this process appears to be very popular, and unlike the generally depressed market situation in British Columbia at the present time, this mill can sell all the pulp it can produce. Clearly, owing to the fact that elevated temperatures are used in the process, there is a distinct possibility that certain constituents binding the wood fibres together can be dissolved and released into effluent discharged into the receiving stream. This is one area that requires investigation at the present time, and I understand that Dr. Jim Servizi at the Sweltzer Creek Laboratory of the International Pacific Salmon Fisheries Commission is doing just that.

Groundwood pulp has never been subjected to the same kind of intensive bleaching process as kraft pulp, because it is mainly used for newsprint, where the permanent whiteness of the paper is not as important as in other pulp products. In the past, zinc dithionite (known as "zinc hydrosulphite" in the trade) has been used as the conventional brightening agent for groundwood. Unfortunately, it was found in the early 70s that high concentrations of zinc were appearing in oysters near pulp and paper mills which were producing newsprint and using zinc dithionite as a brightening agent (Fig. 3). In 1973, the pulp and paper industry in British Columbia voluntarily switched to a different brightening agent for groundwood, sodium dithionite. Because this chemical is made by the so-called Borol process using sodium borate, we were somewhat concerned that unduly high concentrations of boron might be released into receiving waters. Fortunately, the levels of boron to be introduced into the ambient marine environment, over and above the concentrations already there, turned out to be ecologically inconsequential.We have not identified any problems associated with use of sodium dithionite as a groundwood brightening agent (Environment Canada 1973; Thompson et al. 1976).

## 4. CHARATERISTICS OF EFFLUENT THAT AFFECT AQUATIC LIFE

Pulpmill effluents per se cannot be regarded as acutely toxic, highly persistent or capable of being bioaccumulated. On a global basis, it is difficult to become very excited about pulpmill effluents as pollutants. Locally, however,

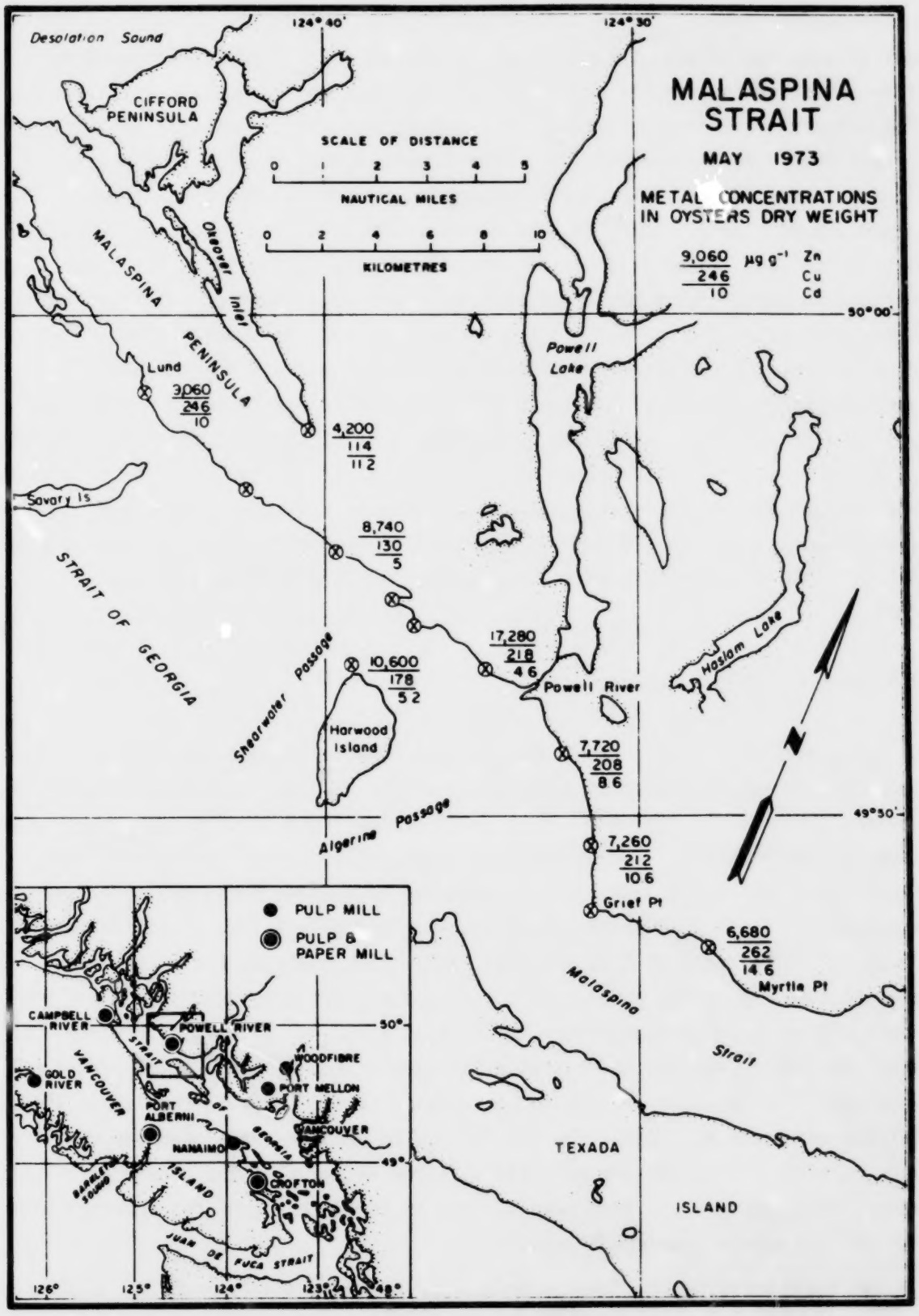


Figure 3. Metal concentrations in oysters, Crassostrea gigas, on the eastern side of the Strait of Georgia in May 1973. Inset shows location of pulp mills around the Strait of Georgia and on the southern half of the west coast of Vancouver Island.

their effects can be devastating. Table 1 summarizes the relative impacts of different effluents from the pulp and paper industry on the aquatic environment. Local effects arise largely because of the large volume[1] of pulpmill effluents and the fact that they are sometimes released into waters with valuable fisheries resources, or which may be used during part of the year at least for spawning (salmon and herring), rearing (juvenile salmonids) or migration (juvenile and adult salmonids). There is a difference in the impact of pulpmill effluents depending on whether they are discharged into streams, estuaries or other coastal waters. This is related in part to the presence of salt in seawater, which generally diminishes the harmful effects of pulpmill effluents to aquatic organisms (Waldichuk 1962a). Millner (1980) described the changes in dissolved oxygen and in benthic fauna caused by the discharge of pulp and paper mill wastes into an estuarine tidal channel on the southeast coast of England. The effects of the pulp and paper industry generally on the aquatic environment have been reviewed by Poole et al. (1978). An excellent review on the effects of pulp and paper mill effluents in the marine environment has been published by Pearson (1980).

## 4.1 Biochemical Oxygen Demand (BOD)

All pulpmill effluents exert a certain biochemical oxygen demand (BOD), but some types of effluents have a higher BOD than others. Spent sulphite liquor undoubtedly has the highest BOD. Kraft mill effluent (KME) has a much lower BOD, because recovery is practised in the kraft chemical process. Two decades ago, effluent from the full-bleach kraft process had an average 5-day BOD ($BOD_5$) of about 100 $mg \cdot L^{-1}$, while spent sulphite liquor (SSL) gave a $BOD_5$ of approximately 1000 $mg \cdot L^{-1}$. The ratio of 1:10 for $BOD_5$ (KME): $BOD_5$ (SSL) probably continues today, if recovery in the sulphite process is not practised, even though the BOD of both effluents has probably been substantially reduced in the last twenty years. The major problems in coastal mills have arisen as a result of dissolved oxygen depletion in waters receiving spent sulphite liquor (Waldichuk 1958, 1966; Waldichuk and Bousfield 1962). No similar low-DO problems have been reported for rivers receiving effluent from pulp mills in the interior of the province; however, no sulphite mills have ever existed in the interior of the province with which one can make a true comparison.

[1] It has been estimated that for every ton of full-bleach pulp produced, 0.242 x $10^6$ L (64,000 U.S. Gal) of water are utilized.

Table 1. Relative pollution effects of pulp and paper mill effluents on different water and sediment characteristics[a].

| Effluent | Biochemical Oxygen Demand (BOD) | Toxicity | Particulate Matter | Metals | Colour | Hydrogen-ion Concentration (pH)[b] | Odour | Foam |
|---|---|---|---|---|---|---|---|---|
| Spent sulphite liquor (untreated) | xxx | xxx | x | - | xx | xx | xx | xxx |
| Kraft mill effluent (unbleached) | xx | xx | x | - | xxx | xx | xxx | xx |
| Bleach plant effluent, caustic extraction | xx | xx | - | - | xxx | xxx | xx | xxx |
| Bleach plant effluent, chlorination | x | xx | - | - | x | xxx | xx | xxx |
| Bleach plant effluent, zinc dithionite[c] | - | x | - | xx | - | - | - | - |
| Groundwood effluent | x | - | xxx | - | x | - | - | - |
| Woodroom effluent | x | - | xxx | - | x | - | - | - |
| Chemical additives for slime, foam control, etc. | - | xx | - | xx[d] | - | - | - | - |

a. Key:-negligible effect; x - small effect; xx - moderate effect; xxx - large effect

b. Mainly in freshwater discharge

c. Groundwood mills in British Columbia no longer use zinc dithionite (zinc hydrosulphite) as a brightening agent. They switched to sodium dithionite in 1973. The effect is mainly in bioaccumulation of zinc by molluscs, e.g. oysters.

d. Mercury in effluents arose from the use of organic mercurial compounds, e.g. phenyl mercuric acetate, for slime control. Such compounds were discontinued in about 1960. Other non-metal-containing slimicides are now used. Mercury residues continue to reside in sediments near pulpmill outfalls. Cadmium also exists in such sediments, but its source is unknown.

Effluent from groundwood mills is comparatively low in BOD, although there are some indications that it may reach a level as high as that exhibited by kraft mill effluent. The fine fibres that escape with effluent from groundwood mills may exert an oxygen uptake of longer duration than that noted for the dissolved organic constituents. Their effect may be of greatest significance in the sediments where the fibres eventually settle.

Pulpmill effluent discharges in the province have often been controlled on the basis of their oxygen demand. The Port Alberni pulp mill, for example, had its production tailored in such a way that the oxygen demand could be satisfied by the receiving water in Alberni Inlet, with enough oxygen remaining for fish survival.

Determination of BOD still presents assorted problems. Because it depends on the action of bacteria in decomposing the organic constituents in effluents, BOD determination depends on the skill and experience of the laboratory technician, and is sometimes regarded more as an art than a science. There is still controversy concerning the seeding with appropriate cultures, for example, particularly samples of contaminated seawater. Razzell (1972) discussed some of the different procedures and pitfalls in BOD determination.

### 4.2 Toxicity

The greatest concern about pulpmill effluent discharged into waters frequented by fish is its toxicity. A highly toxic effluent discharged into a concentration of fish could lead to a fish kill. Fortunately, lethal conditions seldom arise from pulpmill effluents, because the effluent that is finally discharged into receiving waters normally contains only relatively low concentrations of highly toxic constituents, and the discharge is generally directed away from areas frequented by fish.

Standard static or flow-through bioassays are used to determine the 96-hour LC50 (concentration that is lethal to 50% of the test organisms over an exposure period of 96 hours) for the purpose of management of pulpmill effluent discharge. Pulpmill effluents are difficult to work with from the point of view of standardizing against some toxic constituent that can be isolated, identified,

and quantitatively measured. The effluent is usually such a conglomeration of various organic substances from the wood, as well as inorganic salts present in the cooking liquor, that it is almost impossible to select a particular compound and use that as a measure of the toxic moiety in the effluent. Consequently, the practice in the past has been to obtain a 24-hour composite sample, when the mill is under normal operation, and use that as a basis (100% for the undiluted effluent) for measuring the concentration of effluent used in the bioassay.

The really important manifestation of the toxicity of an effluent on an aquatic organism over the long term is the chronic or sublethal effect. This type of stress has been measured in a number of ways, such as effect on blood characteristics, circulation, cough response, avoidance behaviour, growth, and swimming performance. Sensitive techniques are required to measure responses at the subacute level, particularly at the threshold concentration above which a distinctive response is elicited and below which there is no effect. Different techniques may arrive at different sublethal response thresholds. For example, Walden (1976) reported a sublethal response threshold of 0.05 of the LC50 for full-bleach kraft-mill effluent, whereas Davis (1976) estimated this to be 0.02 of the LC50. Such a value derived experimentally one way or another has much more validity than the old "application factor", usually chosen quite arbitrarily as 0.1 for multiplying the LC50 by to provide a "safety factor", when evaluating the maximum permissible concentration in receiving waters.

While there have been several recorded events of acute toxicity to aquatic animals from either toxic materials in effluents or from conditions created in the receiving waters, e.g., low dissolved oxygen, there have been few instances when it has been possible to document sublethal effects. Perhaps the best example is the apparent effect of effluent from the Crofton pulp mill (Waldichuk 1964a) on the condition factor of oysters in Stuart Channel (Quayle 1964). Although migrating salmon may suffer from sublethal stress caused by the effluents discharged by numerous mills into the Fraser River, no effort has been made so far to document this stress in any way.

There is a host of organic and inorganic compounds, derived from the wood, process chemicals and from chemical interaction among the various wood products and process chemicals, e.g., chlorination of phenolic organic compounds during

bleaching. Some of these compounds have not yet been identified, and certainly the toxicity of most has still to be determined. A review of what is known about these compounds, especially the organics, is beyond the scope of this paper. Undoubtedly, others in this Symposium will give a good coverage of the many organic compounds present in pulpmill effluents.

Additives for controlling such nuisances as foam and slime may be quite toxic. When sawmills are associated with pulp mills, lumber may be treated by such fungicides as pentachlorophenol, which is quite toxic to fishlife. The significance of the presence of these chemicals in pulpmill effluents as a result of spillage and leaching is unknown. Spills and leaks occasionally occur from plant equipment, such as the PCB (polychlorinated biphenyl) spill that occurred at the Columbia Cellulose Ltd. mill in Prince Rupert. The PCB spill affected sediments in Porpoise Harbour, and as a result, dredge spoils from there could not be dumped in the sea, because PCBs are prohibited from ocean dumping under the Ocean Dumping Control Act.

4.3 Wood Solids

A component of pulpmill effluents that has been sometimes overlooked in the past is suspended wood solids. Although suspended wood particles do not appear to be acutely toxic to fish (Werner and Robinson 1978), they undoubtedly lead to sublethal stress by causing the fish to clear their gills continuously to keep them from clogging with wood particles. These particulate materials eventually settle on the bottom of receiving waters, moreover, and adversely modify the benthic habitat. This may consist of a layer of fibres, wood chips and bark on the bottom downstream from an outfall (Werner 1965; Werner and Hyslop 1968a), where bottom organisms may find it unattractive to settle and live, or it may be an actual sludge bed that decomposes and generates methane, hydrogen sulphide, and other noxious gases (Werner 1968; Werner and Hyslop 1968b). Decomposing wood fibres remove oxygen from the sediments and overlying water. This may be an important factor in the oxygen balance of a slow-flushing shallow-water system. It was found to be the case in Alberni Harbour, for example. Fibres and other wood solids deposited on salmon spawning grounds in streams can virtually eliminate production on such grounds, because of reduced permeability of the gravels, decomposition of the wood fibres, and resulting low-oxygen concentration,

or even anoxic conditions, in the gravel water.

In general, the ecological impact of wood solids is inversely proportional to their size. From this point of view, fibres are perhaps the worst offenders. With a large surface area-to-volume ratio, they offer a great deal of surface on which bacteria can feed and grow. Sludge beds of accumulated wood fibres exhibit high hydrogen sulphide concentrations which allow no marine life except anaerobic bacteria and fungi to survive. The head of Cousins Inlet at Ocean Falls is a classical example of such fibre deposition. It is uncertain what impact larger pieces of wood have on the marine benthic ecology over the long term. Deadheads and other large chunks of wood sometimes serve as a substrate for settlement of certain benthic species and as shelter for fish and invertebrates from predators.

Efforts are now being made in all pulp and paper mills to reduce the amount of wood solids released in their effluents. Provincial regulations under the Pollution Control Act and federal guidelines under the Fisheries Act set upper limits on the concentration and total amount of wood solids present in these effluents. Clarifiers have been installed at a number of coastal mills to remove larger wood solids from woodroom operations. The collected solids are often dried and used as hog fuel in the plant for energy. Settling ponds are commonplace at interior mills to allow finer wood particles, such as fibres, to be settled out of the effluent before discharge. The settled sludge from these ponds finds little use and must be disposed of in landfills, or incinerated after some preliminary dewatering and drying.

### 4.4 Metals

Of the various substances arising from pulp and paper production, metals are considered to present the most serious long-term concern. Heavy metals are normally not regarded as being present in high enough concentrations in either the wood or processing chemicals to give cause for concern. They arise from the use of metallic compounds as brightening agents, chemicals for slime control and possibly from leaching of metal corrosion products in the plant.

4.4.1 Mercury. Mercurial organic compounds (e.g., phenyl mercuric acetate) have been used in the pulp and paper industry to suppress bacterial slimes. They

were found to be particularly effective in controlling slimes associated with paper making. Around 1960 the pulp and paper industry in British Columbia voluntarily discontinued the use of mercurial organic compounds for the control of slimes in their plants. This action was taken because the Food and Drug Administration of the U.S.A., where much of Canadian pulp and paper is exported, established regulations that prohibited any mercury residues whatsoever in paper products, in order to avoid any possibility of mercury contamination of human food by paper packaging and wrapping. Thus, mercury residues from slimicides ceased to be discharged into receiving waters of British Columbia after 1960. Less offensive and less persistent chemicals replaced the mercurial slimicides.

This action, however, did not alleviate the problem of mercury residues in sediments that had already been created by the earlier use of mercurial slimicides. The problem became particularly apparent after promulgation of the Ocean Dumping Control Act in 1975, with regulations prohibiting the dumping of dredge spoils in which mercury concentrations exceed 0.75 $ug \cdot g^{-1}$ (ppm) in the solid phase and 1.50 $ug \cdot g^{-1}$ in the liquid phase. Because dredging must take place regularly in the vicinity of coastal pulp and paper mills, to provide access by freighters to their shipping docks and by tugs to their log ponds, high mercury concentrations exceeding the regulatory limit necessitated finding other means of disposal than ocean dumping for dredge spoils from the waters adjacent to these mills. Fortunately, most of the high-mercury dredge spoils have now been removed.

4.4.2 Zinc. Zinc dithionite (referred to as zinc hydrosulphite in the trade) has been used for a long time in pulp and paper mills for brightening groundwood used for newsprint production. Early consideration of the presence of zinc in pulp and paper mill effluent tended to downplay its potential ecological impact, because of its alleged low concentrations (ca. 1 ppm) in the effluent and expected dilution and dispersion once the effluent mixed with the receiving waters. The potential for bioaccumulation of zinc by certain species was not taken seriously into account at that time, and this turned out to be eventually a major problem. Pacific oysters, Crassostrea gigas, in the vicinity of pulpmill outfalls, were found to have extraordinarily high concentrations (up to 17,280 $ug \cdot g^{-1}$ dry weight) of zinc (Environment Canada 1973; Waldichuk 1974) (Fig. 3).

Again, the industry took the initiative to eliminate this problem and in

1973, the offending pulp and paper mills in British Columbia switched from zinc dithionite to sodium dithionite as a brightening agent. Because the synthesis of sodium dithionite necessitated the utilization of the Borol process, involving sodium borate as a raw material, there was some concern about pollution by boron. Bioassay tests were conducted on phytoplankton, oysters and salmon (Environment Canada 1973). The concern turned out (Thompson et al. 1976) to be unfounded, because of the relatively low concentration of boron in the effluent, when compared to that already naturally present in seawater.

4.4.3 Cadmium. Cadmium is another metal whose concentration in material dumped at sea is controlled by regulations under the Ocean Dumping Control Act. The maximum permissible concentration in dredge spoils is 0.6 $ug \cdot g^{-1}$ in the solid phase and 3.0 $ug \cdot g^{-1}$ in the liquid phase. Concentrations of cadmium exceeding the regulatory limit have been found in the solid phase of sediments adjacent to the pulp mills in Port Alberni and Powell River (Environmental Protection Service, unpublished data). These high cadmium concentrations have created problems for administration of disposal of dredge spoils from both these mills under the Ocean Dumping Contrl Act. Cadmium is normally found in low concentrations in most marine organisms such as oysters and can be bioaccumulated to higher-than-background concentrations when it is biologically available. There is no evidence that Pacific oysters have cadmium concentrations that are higher than background in the vicinity of the coastal pulp mills of British Columbia (Fig. 3).

The source of the cadmium at these mills is unknown. No cadmium-containing chemicals have been identified in either the pulp and paper processing operations or in chemical applications for control of such nuisances as slimes and foams. It is conceivable that cadmium arises from leaching of such materials as cadmium-based paint or cadmium-plated machinery. It is unknown whether such potential sources of cadmium even exist in significant amounts in these mills.

4.5 Colour

Pulp and paper mill effluents normally have a brown, humic-like colour. Sulphite mills discharge effluent with an amber hue caused by the spent sulphite waste,commonly called red liquor. The so-called "white-water" from paper production is, as its name implies, white in colour, resulting from the colloidal

suspension of many tiny fibres. Usually the whitish colour of the white-water is rapidly dissipated into the brown-coloured effluent from pulp processing and caustic extraction in the bleach plant. In kraft mills, the fluid released from the digesters is known as "black liquor" and has high concentrations of lignin, hemi-celluloses, wood sugars, and other organic compounds, as well as salts used in digestion. Most of these materials are utilized for energy by burning and for the contained inorganic chemicals, left in the ash residues of the recovery furnaces. Some of the black liquor, however, escapes in wash waters, although the general practice now is to recirculate the wash water until it becomes sufficiently enriched in black liquor to enable it to be evaporated and burned in the recovery plant.

Most of the brown colour of the effluent from a kraft mill, however, arises from the caustic extraction process in the bleach plant. This effluent is not amenable to enrichment and recovery. It proceeds directly to the sewer or to external treatment. It is alkaline and its colour tends to increase with pH. As it mixes with more acidic effluents and is diluted with receiving waters, its colour diminishes.

The dark brown colour imparted to waters receiving pulp and paper mill effluents presents an ecological problem, as well as being aesthetically undesirable. It inhibits the penetration of sunlight into the receiving waters, and therefore, retards photosynthesis by phytoplankton, seaweeds and rooted aquatic vegetation. Aside from reducing the amount of carbon synthesized, as a source of food in the marine food chain, it also eliminates, or at least diminishes, a source of oxygen in the water. In areas where depleted oxygen, caused by pulpmill effluent, may be a problem, e.g., Alberni Inlet, the oxygen from photosynthesis may be vital for a healthy ecosystem (Parker and Sibert 1973; Sibert and Parker 1973). In most areas, where oxygen depletion is not a serious issue, however, the aesthetic impact of the brown colour may be of greater significance than the ecological effect. The problem has been considered serious enough so that a substantial amount of research effort has been devoted to both the ecological effects of the colour of pulpmill effluent (Parker et al. 1972; Stockner and Cliff 1976; Stockner et al. 1977; Soniassy et al. 1977; Howard et al. 1979) and on methods to remove it (Anderson et al. 1973; Gellman and Berger 1974; Rapson et al. 1975).

One somewhat dubious attribute of the colour of pulpmill effluents is that it provides a tracer for mapping their distribution and movement, either by direct aerial photography (Burgess and James 1970) or by analysis of water samples using the fluorescence of kraft mill effluent (Baumgartner et al. 1971; Almgren et al. 1975; Josefsson and Nyguist 1976; Lundquist et al. 1978), or by the enhancement of the colour of sulphite mill effluent by the nitroso-lignin test (Barnes et al. 1963). It is difficult, however, to identify a specific constituent in pulpmill effluent for which the chemical analysis is not interfered with by natural constituents in water (Nyquist 1979).

4.6 Hydrogen - Ion Concentration (pH)

Pulp and paper mill effluents, because they usually stem from chemical processes utilizing acidic or alkaline chemicals, often have a pH well removed from neutrality. Thus the sulphite process yields an acidic effluent, whereas the kraft process produces an alkaline effluent. Bleachery effluents are alkaline when they come from caustic extraction and acidic when discharged from chlorination. The total composite effluent from a full-bleach kraft mill is normally alkaline, while that from a semi-bleach kraft mill is acidic.

It has often been recommended by pollution-control agencies that the various effluent streams from a pulp mill be mixed before discharge, so that as much neutralization as possible can be achieved. Pulpmill personnel are sometimes reluctant to do this because a foam problem is created, particularly when the acidic chlorination stream is mixed with the alkaline caustic extraction stream. In discharging pulp and paper mill effluents into seawater, the pH of the effluents is rapidly adjusted to that of the ambient seawater as mixing takes place, because of the high buffering capacity of seawater due to the weak-acid salts it contains. Freshwater, on the other hand, does not possess this capacity. When non-neutral effluents are discharged into freshwater, adjustment of pH is essential prior to discharge. Otherwise, the receiving waters may end up alkaline or acidic, depending on the pH of the effluents. It is now well known that the toxicity of pulpmill effluents is often increased considerably by departure of the pH from neutrality and this has to be taken into account in bioassays on pulpmill effluents (Betts and Wilson 1966; Betts et al. 1967; Davis and Mason 1973; Walden et al. 1975; Walden 1976).

4.7 Odour

Pulpmill effluents and atmospheric emissions are notorious for their offensive odour. Kraft mills are particularly characterized by an unpleasant smell because of the sulphides and mercaptans that are present. For humans, this is a definite amenity interference if not an actual health problem. What kind of a problem does it pose for aquatic life? Does it affect migrating salmon, for example, which derive at least some of their clues for direction to their home stream by olfaction? Does it affect chemoreception in other ways, such as that presumably utilized for mate and food searching? These are still essentially unanswered questions. Brett and McKinnon (1952, 1954) tested unbleached kraft mill effluent from the Port Alberni pulp mill, along with 53 other substances, on adult coho and chinook swimming up a fish ladder that by-passes Stamp Falls on the Stamp River during September - October 1952. They found no significant repellant action in this effluent even though it was tested in quite high concentration by dumping 19 litres of the undiluted effluent into the water flowing over the fish ladder at 0.79 $m^3$ $sec^{-1}$ (28 $ft^3$ $sec^{-1}$).

There has been some speculation on the part of fisheries officers that pulpmill effluent has affected spawning migrations of salmon. For example, when the Gold River pulp mill went into operation in 1968, there were said to be delays in the spawning migrations of coho to the Burman River at the head of Muchalat Inlet and of the large chinooks (tyee) migrating to the Gold River. It was suggested that this could pose management problems for the tyee particularly, because the permits to fish these large salmon were granted for a relatively brief period when they were expected, based on historical records, to be present in Muchalat Inlet enroute to their spawning grounds. Whether in fact there has been an effect of the Gold River pulpmill effluent on the spawning migration in Muchalat Inlet has never been verified. It is conceivable that an effect occurred initially, but that the fish gradually became acclimated to the pulpmill effluent and resumed normal migration behaviour.

Research on causes and abatement of odours in pulpmill effluents has been sponsored by the National Council of the Paper Industry for Air and Stream Improvement (NCASI 1950, 1955, 1971a, 1973b). One of the major consumer problems with odoriferous substances in pulpmill effluents is the impairment of flavour of

fish products (Dymond and Delaporte 1952; Tamura et al. 1954; Shumway and Chadwick 1971; Shumway and Palensky 1973).

## 5. ENVIRONMENTAL CONSIDERATIONS

Environmental characteristics can make a very large difference in the way that a given volume of pulpmill effluent with particular characteristics will affect the waters into which it is discharged. A stream with a small, slow, quiescent flow will be much more adversely affected than a large stream with a swift, turbulent flow. Similarly, on the marine side, a poorly-flushed, shallow inlet will become far more polluted than a tide-swept channel or an exposed open coast, by receiving the same volume and type of pulpmill effluent. Freshwater and seawater are affected in different ways by pulpmill effluent, and this difference stems mainly from the fact that the former has little or no salt, while the latter contains assorted salts up to a concentration of about 3.5% (Waldichuk 1962a). It is the salt content of the seawater that gives it the buffering capacity and reduces the toxicity of most constituents present in pulpmill effluents.

### 5.1 Riverine Conditions

Streams that undergo large seasonal fluctuations in flow, with very low flows in the summertime, are extremely vulnerable to the harmful effects of pulpmill effluent. Aquatic life cannot be expected to survive during the low flows, because of the high concentrations of pulpmill effluent that occur at that time, as a result of low dilution. High temperatures that usually accompany summertime, low streamflows further exacerbate the highly toxic conditions. Dissolved oxygen can be depressed to a minimum in the river when the streamflow is small and the water is warm, partly because the solubility of oxygen decreases with increasing temperature and partly because the respiratory consumption of oxygen by microorganisms increases with temperature.

Large streams, such as the Columbia and Fraser rivers, can accept pulpmill effluent without serious ecological damage much more readily than the small streams. It is mainly a case of greater dilution. Generally being quite turbulent, these streams not only mix the pulpmill effluent rapidly into their waters but also become continually oxygenated by aeration. Consequently, there

has seldom been a problem of low dissolved oxygen arising out of pulpmill effluent disposal into the Columbia and Fraser rivers. Being glacially-fed, these rivers have temperatures that remain comparatively low the year around, except for some of the lower stretches of the Columbia, which have been dammed for hydroelectric power, and the retained water is exposed to continuous solar heating during the summer.

The high silt load of glacially-fed streams is a factor that probably ameliorates the adverse ecological effect of substances present in pulpmill effluents. Some of the harmful constituents are probably adsorbed onto the particulate materials in the river water and eventually deposited in the sediments. Moreover, the high natural turbidity conceals the brown colour of the pulpmill effluent, and the effect is not as unsightly as it is in clear water, nor is its relative ecological impact as great in reducing light penetration and photosynthesis.

## 5.2 Coastal Conditions

Coastal areas in British Columbia receiving pulpmill effluents have been classified (Waldichuk 1962a, 1962b, 1968) into three categories, based on shoreline configurations and rate of flushing: (1) Inlets, (2) Partially-enclosed embayments; and (3) Tide-swept channels.

5.2.1 Inlets. A considerable proportion of pulp and paper mills in British Columbia are located on inlets. These natural marine canal systems penetrating deep into the interior of the mainland of the province and Vancouver Island are attractive for pulpmill installations, because they are near sources of wood supply, water and power and usually have a deep, protected harbour for transporting and holding logs and for shipping their products abroad. There is often a moderate-sized river draining into the head of an inlet and numerous smaller streams draining into the inlet from both sides between its head and its entrance. This runoff is what provides the mechanism for transporting the effluent at the surface from the outfall to the sea. The freshwater inflow generates a seaward current in the surface layer and the pulpmill effluent can be carried to sea by this flow. Inlets with only a small inflow of freshwater at the head, such as Neroutsos Inlet, do not experience the same degree of surface

flushing as inlets with larger tributary streams, e.g., Alberni Inlet. Pollution can become acute in inlets with small freshwater runoff if there is a large surface input of pulpmill effluent.

5.2.2. Partially-Enclosed Embayments. This category of coastal bodies of water is exemplified by the numerous harbours on the east coast of Vancouver Island, where embayments are often protected by barrier islands, providing good shelter for ships, but inhibiting free exchange of waters with the Strait of Georgia. Depending on how wide the water connection is between the embayments and the open bodies of water adjoining them, these embayments may be flushed reasonably rapidly or very slowly. Outfalls for pulpmill effluent and for municipal sewage are usually placed outside the protective barrier islands, if such exist, in order to provide more rapid dilution and dispersion of the effluent, e.g., Crofton (Waldichuk 1964a) and Prince Rupert (Waldichuk 1966) pulp mills.

5.2.3 Tide-Swept Channels. Channels in which the tidal current is swift and the flow is turbulent provide the best coastal environment for effective effluent disposal. Dilution and dispersion are rapid. The rate and degree of assimilation are only limited by the volume of clean water that is introduced on each tidal cycle. By far the best example in British Columbia of pulpmill effluent being released into a tide-swept channel is the pulp mill at Duncan Bay discharging into the swift and turbulent waters of Discovery Passage. There is extremely rapid dilution and dispersion in this vertically- and horizontally- mixed system. A considerably slower rate of dilution and dispersion is offered the effluents from the pulp mills at Harmac and Powell River, discharging into Northumberland Channel and Malaspina Strait, respectively, but these systems can also be placed in the category of tide-swept channels.

## 6. OPTIONS IN SELECTING SITES AND MODES OF EFFLUENT DISCHARGE FOR PULP MILLS TO MINIMIZE ENVIRONMENTAL AND ECOLOGICAL IMPACT.

It has been some time since a site was selected for a new pulp mill in Biritsh Columbia, and what is said in this section may not be too relevant at present. When new pulp mills were being installed, however, the mistake was often made by industry of acquiring the real estate before advising regulatory

agencies of the plan to build a mill. By being locked into a particular mill location, the flexibility for selecting a desirable outfall site may be lost. This may not be as important in selecting a suitable location for a pulp mill on a given river as it is in siting on the coast.

## 6.1 Factors Affecting Dilution and Dispersion

It is clear that when a pulp mill is being planned to be sited on a river, one must examine the seasonal discharge and then calculate the expected concentration of effluent and total oxygen demand compared to available oxygen at minimum flow. If the oxygen supply does not meet the oxygen demand, and leave sufficient oxygen for fish life, then one must seek either a larger river for effluent disposal or apply a higher degree of treatment of the effluent in order to reduce the BOD. This applies also if the predicted toxicity of the effluent in the river water does not meet the requirements for aquatic life.

If discharge of the effluent is planned for coastal waters, then the evaluation of the environmental and ecological impacts is somewhat more complicated. A number of factors must be considered: current speed and direction; rate of mixing; and amount of exposure to the effects of winds, tides and runoff. Strong currents and intensive mixing are obviously important criteria for rapid dilution and dispersion. Discharge of effluent into eddy systems must be avoided if the effluent is to be transported rapidly out of the area and not retained in some nearshore gyre. The volume of water that passes in a given time through the area where the outfall is to be sited is an important factor, of course, since it determines the amount of dilution and dispersion that will be afforded the effluent. It is essential to note also if the same water moves repeatedly through the proposed outfall area, as in the case of tidal action moving the same body of water back and forth in an inlet, or an eddy recirculating essentially the same water in an embayment. Experience has shown that it is best practice to release effluent off the most seaward projection of land, usually a point or promontory, in order that the effluent is caught in the mainstream tidal current and transported out of the area.

6.2 Presence of Fisheries Resources

In virtually all cases of disposal of pulpmill effluent into fresh or marine waters, the presence of fisheries resources is a foremost criterion in the evaluation of the suitability of a given site for an outfall. Is the area an important migration route for salmonids? Are there noteworthy spawning grounds for salmon or herring in the vicinity? Is it a vital nursery ground for juvenile salmon and trout? How important is it as a commercial and recreational area for shellfish? Can it be regarded as a significant wildlife refuge? All these living resources must be taken into account, and each has its specific requirements for habitat and water quality. While the surface discharge of pulpmill effluent in a coastal area of large freshwater runoff may not present a too serious hazard for salmonids, it may be devastating for oysters, which would be continually bathed by the effluent. Shrimp grounds may be vulnerable to the accumulation of fibres and other solid wood fragments on the bottom, inasmuch as shrimps are sensitive not only to the decline in dissolved oxygen that such accumulations would induce but also to the change in substrate. Deposition of fibres in gravel used by spawning salmonids could lead to permanent destruction of spawning grounds, inasmuch as the permeability of the gravel to water percolation is adversely affected by a fibrous mat, and the decomposition of the fibres depletes the dissolved oxygen in the gravel water that bathes the salmon eggs.

In general, the presence of fisheries resources in an area designated for pulpmill effluent disposal will demand the utmost in efficient recovery in the mill and the fullest treatment of the effluent prior to discharge. Proper location of the outfall and design of a diffuser system for rapid dilution, dispersion and transport of the effluent by currents out of the area can ameliorate the adverse effects to some extent, but this cannot be a substitute for treatment of the effluent, if the volume of water available for dilution is inadequate to meet water quality criteria for aquatic life.

6.3 Mode of Discharge

Assorted ways have been used in the past to rid a pulp mill of its effluent. In the early days, the easiest way, and this approach was often used, was to dig a ditch and let the effluent drain to the nearest water course, whether this be a river or a coastal channel. Sometimes, various streams of effluent would just be allowed to meander through a marsh and find their way to the seashore. This

actually happened with the early installation of the pulp mill in Port Alberni in 1949, when effluent was allowed to drain in an uncontrolled way through the marshes of Lupsi Cupsi Point before reaching the northeastern corner of Alberni Harbour. The company eventually "corrected" this situation and dug a ditch to collect all the mill effluent streams and discharge the total effluent directly into the mouth of the Somass River, creating a situation which was not exactly appealing to the local fisheries officer, to say nothing of the appeal to the juvenile and adult salmonids migrating through the area. Needless to say, the situation had to be corrected as quickly as possible. This was done by installing a flume to carry the effluent away from the river mouth and into the seaward flow of the river water flowing over the seawater in the harbour, as recommended by Tully (1949).

More direct routes to the sea were used by such mills as the one at Harmac, near Nanaimo, which is located right on Northumberland Channel and went into operation in 1950. It had rather short effluent lines which discharged intertidally at the northern end of its deepsea wharf. A foam boom kept large chunks of stiff foam, formed by the turbulent cascading of effluent into inshore surface seawater, from escaping into Northumberland Channel. That was the sum total of the engineering design for the outfall until the deep-sea diffuser was installed in the 1970s.

I recall that it was a big shock to both the company building the mill and the design engineers when we asked that the outfall for the pulp mill planned for Crofton in the late 1950s not only be taken from shore but be carried beyond the Shoal Islands to a depth of 10 fathoms (18.3 metres) and terminate in a diffuser (Waldichuk 1964a). Most coastal pulp mills now either already have a submarine outfall with a diffuser or are installing one. Interior mills in almost all cases have an outfall that consists of a pipeline equipped with diffuser ports laid along the bottom across a stream, normal to the direction of streamflow, in order to achieve the most rapid dilution and dispersion.

### 6.4 Physical and Chemical Characteristics of the Receiving Water

The physical and chemical characteristics of the receiving water are important when one estimates its assimilative capacity. The natural dissolved

oxygen concentration, for example, will determine the extent to which the oxygen demand of the pulpmill effluent can be met and still leave sufficient oxygen for fishlife. The introduction of other industrial or municipal wastes upstream in either a river, estuary or coastal waters may already substantially tax the natural oxygen supply and general assimilative capacity of the receiving waters.

Whether a stream is clear or turbid will determine the degree of treatment (colour removal) that may be required to meet aesthetic requirements, if not ecological water quality criteria. Streams that undergo excessive seasonal warming may not be able to tolerate additional heat from pulpmill effluents during the summer. Either the effluent has to be ponded to cool it, or a more appropriate choice of a stream, lake or coastal body of water with lower temperatures has to be made to overcome the summertime warming problem. A stream that has a low pH, because of acid precipitation, may suffer greater adverse effects than one with neutral pH, if the total effluent from a pulp mill is acidic.Although this has not occurred in British Columbia so far, the pH problem is one that must always be taken into account when designing treatment facilities for a pulp mill and choosing an outfall site.

## 7. TYPES OF TREATMENT AND NEEDS FOR THEM

There is a variety of treatments for pulpmill effluent that range from coarse screening to remove larger pieces of wood to advanced treatment that leaves the effluent virtually free of all its undesirable characteristics. The simplest and sometimes the most profitable form of treatment is recovery of lost product. After all, the materials that are lost and discharged to the sewer all had to be purchased in the first place, and the more of the materials recovered before they get into the waste streams, whether it be fibre or turpentine, the greater should be the profits.

### 7.1 Wood Solids Removal

The most primary form of treatment of pulpmill effluent is removal of wood solids. This is sometimes done with mechanical clarifiers, but more often now it is carried out with settling ponds. The wood recovered by clarifiers can be dewatered, dried and burned as hog fuel. With the present-day high cost of

power, hog fuel derived in this way can be a valuable source of energy. The sludge from settling ponds is still generally regarded as a liability in that it must be disposed of by other means than by burning as hog fuel.

Certain inplant facilities prevent losses of fibres and other wood solids. Save-alls have been used to collect fibres from the effluent and screens are still useful devices for removal of coarser pieces of wood and bark. Aside from economic benefits from preventing losses of wood in its various forms, there are now provincial and federal regulations setting limits on both the concentrations of wood solids in pulpmill effluent and on the total permissible wood loss per ton of pulp produced.

### 7.2 Biobasins

Secondary treatment of pulpmill effluent usually involves 5-day impoundment of the effluent with aeration to reduce both the BOD and toxicity (Servizi and Gordon 1972, 1973). Microalgae and bacteria actively decompose organic constituents that may possess a high BOD as well as being toxic to fishlife. In order to maintain a culture of these microorganisms, it is sometimes essential to add inorganic nutrients, e.g., nitrogen- and phosphorus- containing fertilizers, to the effluent in the biobasins. Most interior pulpmills in British Columbia now have biobasins for secondary treatment of their effluents. Some of the more refractory compounds in the effluents, such as resin acids and chlorinated phenols, however, are not substantially degraded in ordinary biobasins, and other treatment is necessary to destroy these substances.

### 7.3 Other Treatments for Specific Needs

A host of in-plant treatments is available for removal of certain undesirable characteristics in pulpmill effluents. These range from foam control to colour removal.

7.3.1 Foam Control. The surface-active characteristics of many components in pulpmill effluents lead to foaming. Sulphate soaps in kraft mills are highly surface-active. Lignin sulphonates discharged from sulphite mills cause foaming in receiving waters, and one could often identify spent sulphite liquor in

seawater by the windrows of foam that are created by tidal turbulence and wind mixing. Foam is aesthetically unattractive in that it usually implies some form of pollution. It can also have ecological implications in that toxic constituents are often concentrated in the foam, and foam that has drifted onto shellfish beds, e.g. oysters, is not expected to yield any benefits (Waldichuk 1964a). But it is not usually the foam in the receiving waters that mill management and technical personnel are concerned about. It is the foam in the plant that causes the greatest nuisance. For example, the foam problem became so acute at the Port Alberni mill during an expansion in the mid 1950s that the mill workers could not find the door to one of the buildings as a result of "mountains of foam" in the yard. A pulpmill manager in Northern Ontario once reported that they had "lost" two railway tank cars of chlorine in their plant yard. The tank cars eventually emerged through the foam that had accumulated on the grounds.

Assorted anti-foaming agents are used in pulpmill operations to control foam. Efforts are made not to combine effluent streams that foam on mixing, e.g., the caustic extraction and chlorination effluents from the bleach plant. The foaming potential of different effluent streams in a kraft pulp mill has been reported (Waldichuk 1964b). It was noted in the foregoing study that the green liquor dregs, from reutilization of the residual salts from the black liquor recovery furnace in a kraft mill, provide an excellent foam-suppressing agent, with 1 ppm sufficient to actively suppress foam produced by other components of the mill effluent.

Foam tanks are sometimes included in effluent-disposal systems for kraft mills. The objective of these foam tanks appears to be to collect the foam formed when various effluent streams are mixed on their way to the outfall. Then efforts are made to collapse the foam by spraying water on it or even using ultrasonic generators. If the foam is successfully collapsed into the effluent, it eventually emerges again on the water surface above the outfall. It would seem more appropriate to skim off the foam and then collapse it in another tank and pipe the resulting liquid back to the recovery plant. After all, the foam collects organic material that is toxic (e.g., resin acids) and has a high BOD. It should be noted, however, that an attempt made to use foam production as a sole form of treatment for a pulp mill in Thunder Bay, Ontario, was not too successful.

7.3.2 Colour Elimination. In areas where the water is clear, the presence of

pulpmill effluent is always evident from the brown colour. This has its aesthetic drawback as well as ecological consequences. Although the constituents in kraft mill effluent that impart the dark colour are largely innocuous lignin fractions that have been variously modified in the digestion process, they provide the visual, tell-tale evidence of pulpmill pollution. From the technical surveillance point of view, the colour has provided a useful tracer for following the movement of kraft mill effluent both by aerial photography and by ship sampling and sample analysis (Baumgartner et al. 1971) or by in situ fluorescence probes. There is interference in any such tracing endeavours from natural humic substances, which look the same and chemically behave similarly to kraft mill effluent.

The cost/benefit ratio in colour removal is usually quite high. Unless aesthetic effects are vitally important, the cost of removal of colour from pulpmill effluent generally cannot be justified by the benefits. Ecologically, there are few areas where the colour of pulpmill effluent has been shown to seriously disrupt the ecosystem, except possibly in waters like those of Alberni Harbour, where the lowered photosynthesis can cause a significant reduction in the oxygen supply (Parker and Sibert 1973; Sibert and Parker 1973). In waters where recreational values are high, particularly in lakes and rivers, there may be justification for colour removal from pulpmill effluent. This applies in British Columbia, if one places a high enough value on aesthetics, to the clear waters of the Thompson River downstream from the pulp mill in Kamloops.

There are various ways to remove colour from pulpmill effluents (Gehm 1973), none of which is particularly simple and inexpensive. Colour can be absorbed by activated carbon, ion exchange resins, various minerals and by the soil. In all cases, the sorbent must be replaced or regenerated for reuse at considerable cost. Lime can be used to precipitate the coloured solids contained in spent caustic extract. There remains the problem, of course, of disposal of the sludge from such precipitation. Activated sludge treatment can remove up to one-third of the colour from kraft pulping effluents, but it is ineffective when bleachery wastes are present. Ion exchange resins appear to be the most promising for effective colour removal, but there is a need for an efficient, inexpensive resin to process the large volume of effluent involved in a typical, moderate-sized (500 tonnes per day) full-bleach kraft mill.

The National Council of the Paper Industry for Air and Stream Improvement, Inc., has supported a considerable amount of research (NCASI 1962, 1970a, 1970b, 1971b, 1973a, 1974; Gellman and Berger 1974) on colour removal from pulpmill effluents. Other investigations (Rapson et al. 1975; Kennedy 1974; Anderson et al. 1973) have examined the use of lime to flocculate colour bodies and the use of ion exchange resins, particularly Amberlite XAD-8, in an absorption decolourizaton process.

7.3.3 Nutrient Control. As a rule, there is little nutrient of the conventional type, e.g, phosphate and nitrate compounds, that originate in the pulp production or bleachery processes. Nutrients, however, may be introduced into the biobasins to promote vigorous bacterial and microalgal growth in the pulpmill effluent, in order to reduce the BOD and toxicity. Sanitary sewage may be mixed with the pulpmill wastes in some mills and this can add nutrients to the effluent. Residual nutrients released with the treated effluent from the biobasins may cause nutrient enrichment and algal problems downstream in the receiving waters, as appears to have occurred in the Thompson River downstream from Kamloops. Control of such nutrient enrichment should be possible with better stoichiometric evaluation of nutrient requirements in biological treatment and in fuller utilization of the added nutrients in the biobasins, perhaps by adding additional biobasins in tandem to continue growth of microalgae until the nutrients are exhausted.

7.3.4 Control of Pathogenic Microorganisms. In the recent decade or so there has been concern about pathogenic microorganisms, particularly of the Klebsiella strain, in pulpmill effluents (Menon and Bedford 1973). Such organisms have been identified in pulpmill effluent and there has been some fear that Klebsiellae and other coliform organisms may be proliferated in aeration lagoons. Faecal coliforms can be introduced into pulpmill effluent, of course, if the plant's sanitary sewage is combined with effluent from the mill processes for discharge into nearby receiving waters.

In the study reported by Menon and Bedford (1973), which dealt with the Fort Frances Pulp and Paper Mill in Ontario, the majority of the coliforms isolated from the kraft mill effluents and aeration lagoon were Enterobacter strains. A small number of Klebsiellae were also isolated, and they were shown to be

pathogenic to mice. Although the public health significance of exposure to Klebsiellae in polluted water had not been determined at that time with comprehensive epidemiological studies, there was sufficient concern about these microorganisms in the pulp and paper industry that some studies were even conducted on Klebsiella in pulpmill effluents of British Columbia (Duncan and Razzell 1972). The status of this problem at present is unknown to this writer. Without any direct evidence that microorganisms in pulpmill effluents are a human health threat, the flurry of concern in the early 1970s appears to have blown over.

7.3.5 Closed Systems for Pulp Mills. Ideally, for water pollution control, it is desirable to have a completely closed system in a pulp mill so that all wastes and residues are used or recycled. This means that everything that remains after the pulp and paper are produced would be recovered either for by-products, energy or for reutilization in the process. There has been little attempt to produce by-products from the kraft process, except for tall oil and turpentine. In the sulphite process, a number of endeavours have been made to produce ethyl alcohol, adhesives, additives for drilling muds and such chemicals as lignin sulphonates and vanillin from the spent sulphite liquor. Markets for these by-products have never provided a sufficient incentive for the industry to go heavily into production for them, certainly not in British Columbia. The black liquor of a kraft mill is evaporated and burned as a rule for energy and for the residual salts, which can be reused in the digestion of wood chips for pulp. Wood solids can be collected and burned for energy. Water from the various processes, with both the solid and dissolved constituents removed, could be reused. Bleachery effluent, with certain treatment, could be recycled. Theoretically, there would be no need to discharge any effluent at all. Additional water would only be required to make up for losses due to evaporation; and new chemicals would only be added to replace those lost by spillages, volatilization and incomplete recovery of materials from the black liquor.

Such a closed system was ostensibly designed by Professor Rapson and colleagues at the University of Toronto (Rapson 1967, 1974; Rapson and Reeve, 1973; Reeve and Rapson 1974; Reeve et al. 1974). Unfortunately, the system appeared to be far from being "closed" when installed at the Great Lakes Paper Co. mill in Thunder Bay, Ont., during the mid 1970s. When I visited the plant in

1976, it still had a long way to go to achieve the status of a completely effluent-free mill. Although the new mill and Rapson system were not yet operating at the time, a complete materials balance was not expected. It was not possible to completely recycle the water, although a considerable reduction in the total water requirement for the mill had been made and it was anticipated that the quality of the effluent discharged into the Kaministiquia River would be substantially improved.

Whether a more recent evaluation of the Thunder Bay mill has shown better promise for a "closed-cycle" bleached kraft mill in practice is unknown. It is unlikely, however, that the pulp and paper industry in British Columbia will rush in to install such mills unless they are shown to be economically viable. This is a poor time in the economy for the industry to invest risk capital on new developments which have not been fully proven either technically or economically.

## 8. A CASE STUDY OF PULPMILL POLLUTION IN BRITISH COLUMBIA

It is useful to review briefly the water pollution associated with at least one pulp mill in British Columbia to illustrate the kinds of approaches that have been taken to solve particular problems. Alberni Inlet (Fig. 4) is chosen here, partly because I "cut my teeth" on it in early studies of pollution by the pulp and paper industry on the Pacific coast, and partly because there is a long history of investigations on Alberni Inlet, starting with the monumental work by Tully (1949) and a review of enviromental knowledge on the system to 1980 by Morris and Leaney (1980). It was originally proposed to install a sulphite mill at Port Alberni. As a result of Tully's (1949) study, which showed that dissolved oxygen in the Inlet would be unacceptably depressed in summer by spent sulphite wastes from a nominal-sized sulphite mill, and because of changing economics of sulphite pulp vis a vis kraft pulp, the industry installed a kraft mill. It commenced production in 1949.

### 8.1 Location of the Outfall

Tully (1949) had recommended a surface discharge of effluent into Alberni Inlet, so that it would be rapidly carried downstream in the Somass River flow. As noted earlier, the company first merely allowed the effluent to flow through the marshes of Lupsi Cupsi Point into the northeast corner of Alberni Harbour, and

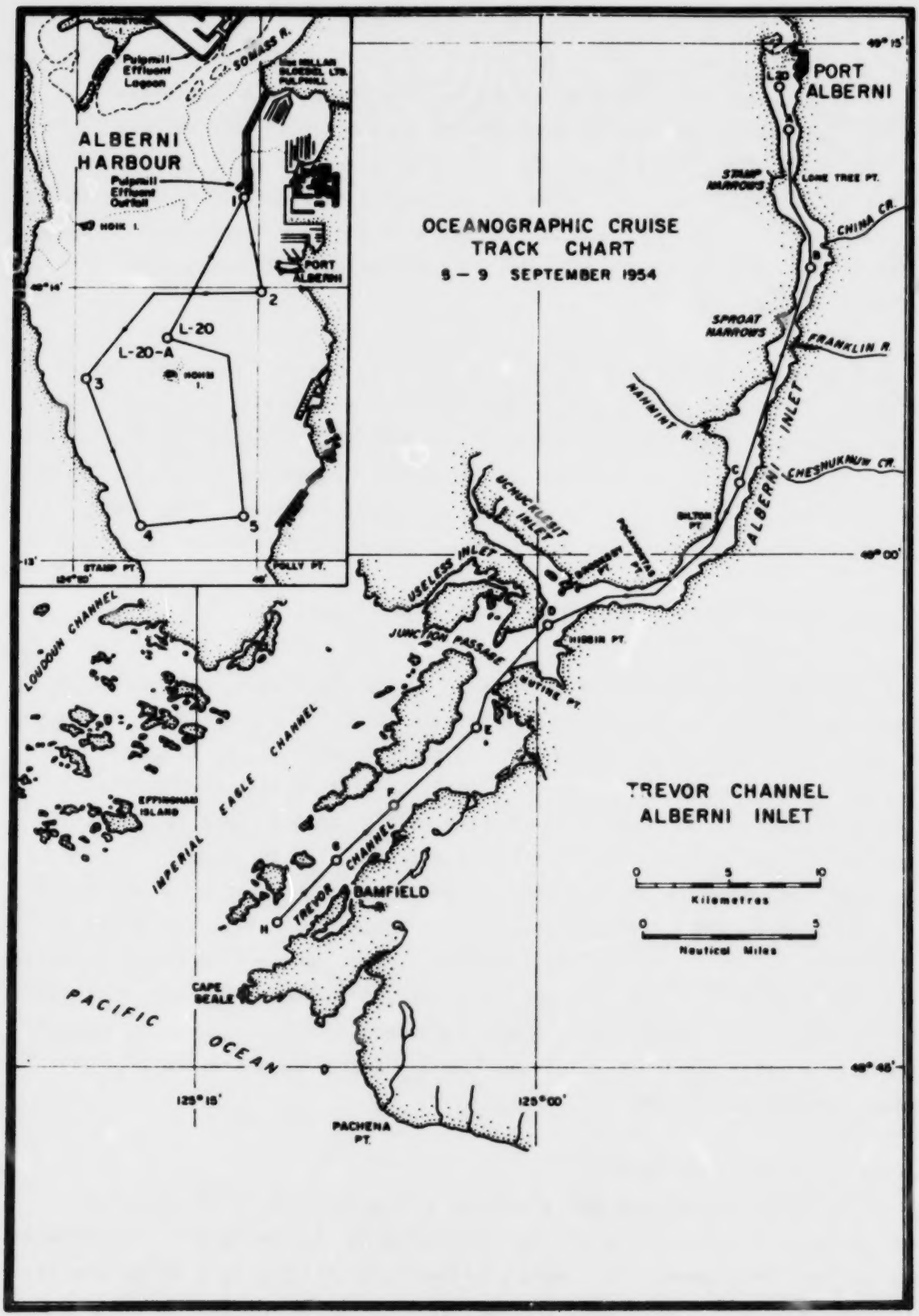


Figure 4. Chart of Alberni Inlet and Barkley Sound, showing the location of the Port Alberni pulp mill and stations occupied in oceanographic surveys during 1954 to 1967.

then in 1956 directed the discharge into the mouth of the Somass River (Fig. 4). Following discovery by the fisheries officer of this undesirable situation, the outfall location had to be corrected. Subsequently, a flume was built to convey the effluent along the deep-sea wharf and discharge it into the harbour at a point where it could be swept into the seaward flow of the jet stream from the Somass River. This system of discharge was retained until the early 1970s, when it was replaced by a new outfall discharging effluent from a biobasin into the northern end of Alberni Harbour.

8.2 System of Pollution Control in the Initial Phase

From some early studies on the toxicity (Alderdice and Brett 1957) and BOD (Greer et al. 1956) of kraft mill effluent, it was determined that dissolved oxygen would be the limiting factor on control of pollution by such effluent in Alberni Inlet. If the requirement for maintaining the dissolved oxygen adequate for salmonids was met, then the acute toxicity problem would be kept under control.

The technique for evaluating the oxygen budget for Alberni Inlet, under the effects of effluent disposal, was essentially as follows: The oxygen uptake per day from the Inlet waters by the pulpmill effluent was evaluated from the 5-day BOD of the effluent. The oxygen uptake by decomposing solid material deposited on the bottom was neglected. The oxygen in the inlet system that would be utilized by the effluent during its decomposition was presumed to be derived mainly from the Somass River water and seawater entrained into the surface layer as the freshwater flowed seaward (Fig. 5). The amount of available oxygen at different discharges of the Somass River, as evaluated by Tully (1949), is shown in Figure 6. The inputs of oxygen from surface aeration and photosynthesis in the inlet, except as included empirically in Tully's (1949) evaluations, were neglected.

The foregoing system of prediction of the effect of kraft mill effluent disposal on the dissolved oxygen concentrations in Alberni Inlet was utilized in determining the allowable production of the Port Alberni pulp mill during the expansion in the 1950s (Waldichuk 1954). It was estimated that the oxygen needed to meet the oxygen demand of the effluent of a 500 tons-per-day full-bleach kraft mill would require a minimum Somass River discharge of 24 $m^3$ $sec^{-1}$ (830 $ft^3$

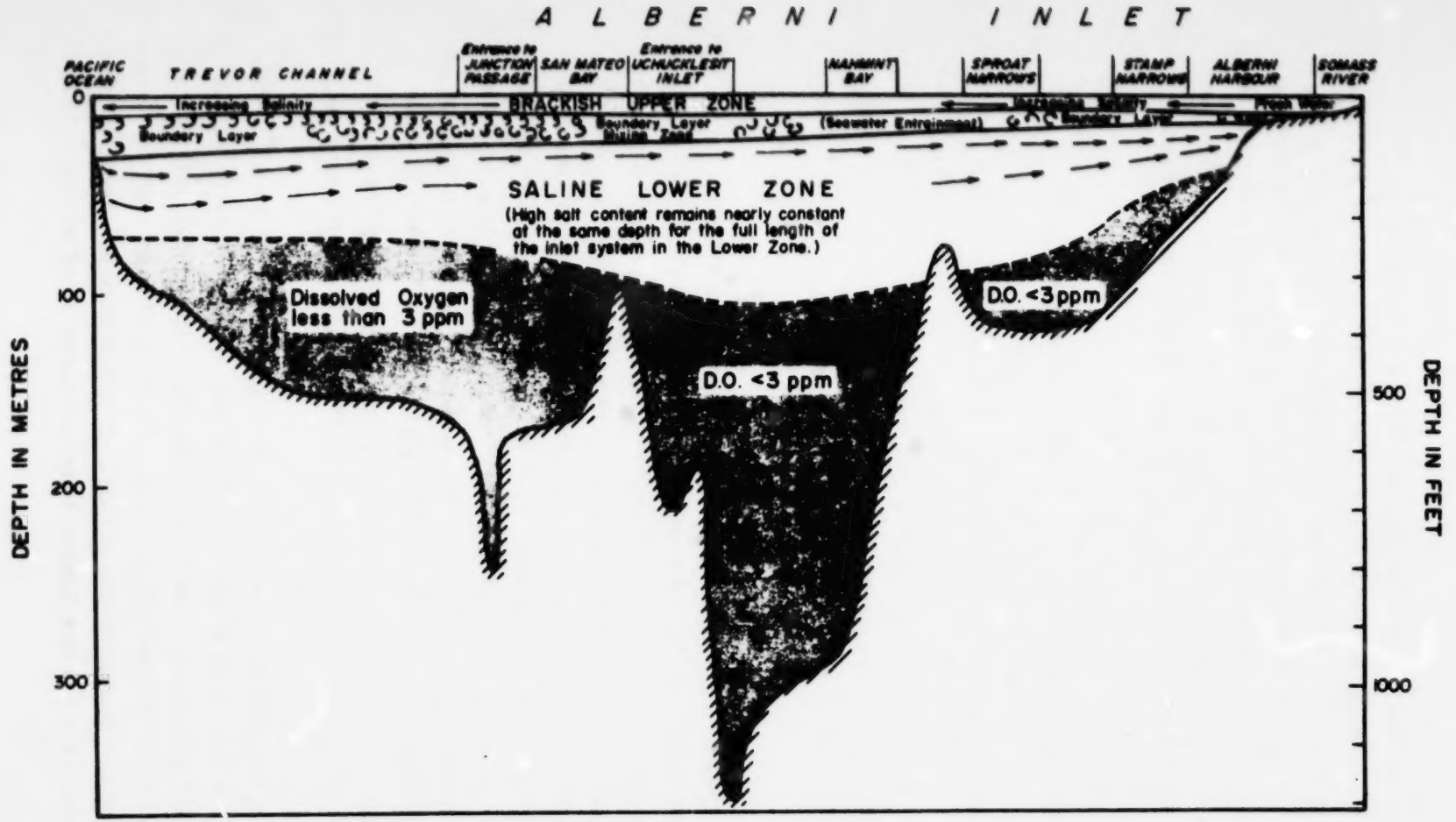


Figure 5. A diagrammatic vertical section through Alberni Inlet, illustrating the salinity structure, deep zone of low oxygen, water movements, and boundary-layer mixing between the seaward surface flow and inward sub-halocline flow.

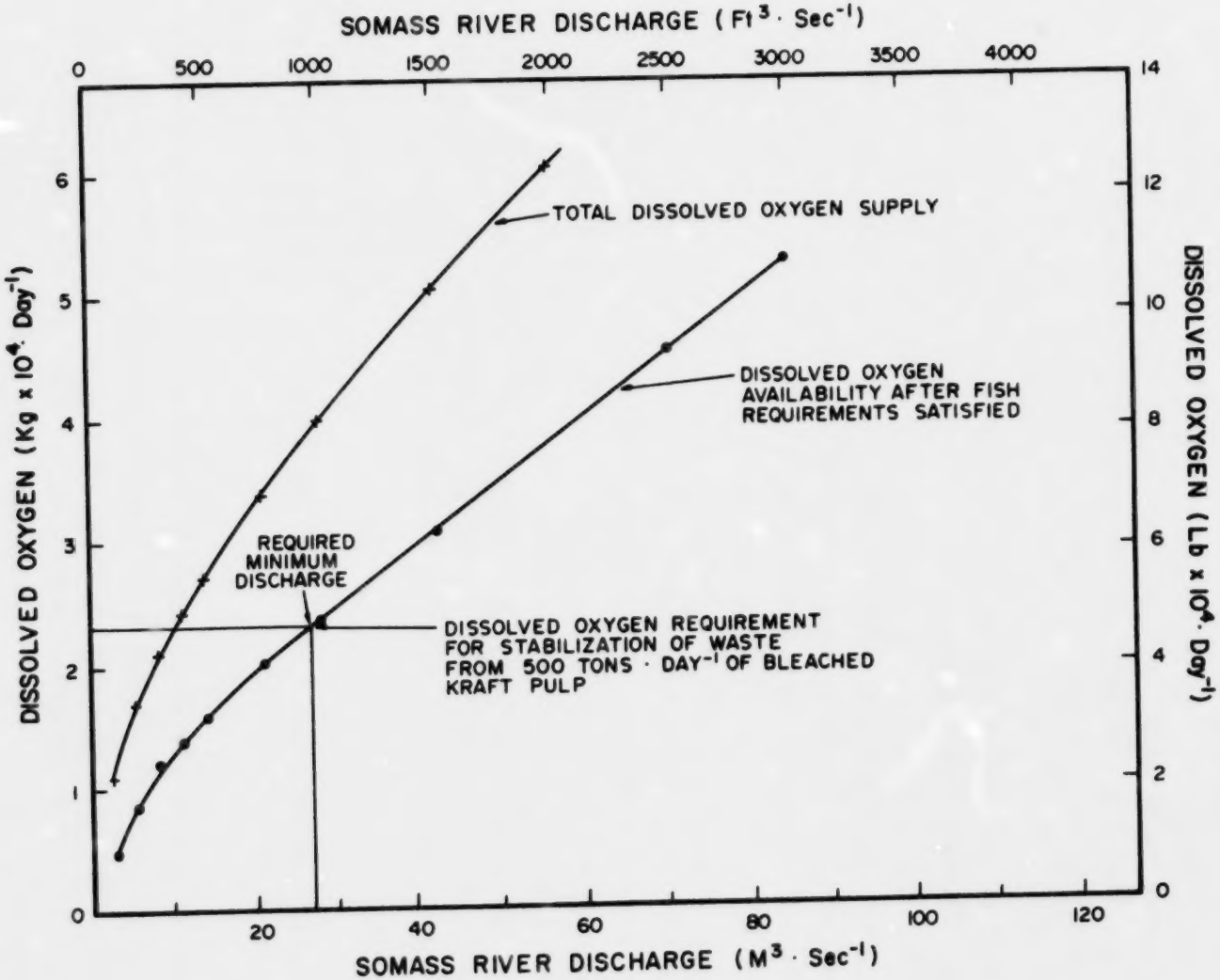


Figure 6. Variation of dissolved oxygen supply in Alberni Inlet with Somass River discharge in late August. Graph shows the river flow needed to meet the oxygen requirement for a typical 500 tons-per-day kraft mill, allowing for a minimum of 40% oxygen saturation in the upper layer.

$sec^{-1}$). Variations in the production volume and type of product changed the minimum discharge requirement in the Somass River according to the volumes and BOD of the effluents. The Somass River discharge was controlled initially by a make-shift dam with stop-logs on the Stamp River, a tributary of the Somass R. This was later replaced by a properly engineered dam with controlled flow at the outlet from Great Central Lake into the Stamp R.

The predictions held reasonably well until 1965, when an unusally warm, dry summer led to dangerously low dissolved oxygen concentrations in Alberni Harbour (Waldichuk 1965; Waldichuk et al. 1968). At that time, MacMillan Bloedel Ltd. were alerted about the critical dissolved oxygen situation in Alberni Inlet and immediately set about to determine the corrective actions that could be taken. It was noted from monthly oceanographic observations in Alberni Inlet (Waldichuk et al. 1968) that during the critical summer period, there were depressions in the dissolved oxygen concentrations in the surface layer from the effluent, as well as in the bottom layer from both natural causes and the effects of decomposing wood solids on the bottom. Salmonids had a relatively thin layer of water in shallow Alberni Harbour, where dissolved oxygen concentrations were adequate for survival, in the "sandwich" between the low-oxygen surface layer and the nearly anoxic bottom layer. Consultants, developing a plan for ameliorative measures in Alberni Inlet (Stanley Associates Engineering Ltd. 1966), estimated that 10% of the oxygen uptake by pulpmill wastes was due to wood solids deposited on the bottom in Alberni Harbour.

### 8.3 Pollution Control with Solids Removal and a Biobasin for Effluent Treatment

Correction of the low-dissolved oxygen situation in Alberni Inlet involved development of treatment systems that would remove solids from the effluent and reduce its BOD. Clarifiers were soon installed for recovery of wood and bark from woodroom effluent. The recovered wood was partially dried and used for hog fuel. Unfortunately, the existing furnaces could not cope with the increased volume of hog fuel, and for a while the wood waste was once again getting into Alberni Inlet, but this time in a slightly charred state as fly ash, to the chagrin of the company and Fisheries officials (to say nothing of the reaction of housewives with drying clothes on lines and automobile owners with cars parked

outside). Fortunately, this situation was soon corrected with larger and more efficient furnaces in the mill. A further clarifier installed by the pulp mill in the area of the Lupsi Cupsi marsh in 1970 allowed removal of 25 tons (22,700 kg) per day of suspended solids from hydraulic barker, groundwood and newsprint effluents. On the west side of the mouth of the Somass R., an aerated lagoon was constructed and went into operation in 1971 to biologically treat the effluents from the woodroom, groundwood, newsprint, kraft pulp, and caustic bleach extraction operations. Effluent from the lagoon is discharged into the north end of Alberni Harbour by way of an outfall near the end of the pulp mill's deepsea wharf.

By all accounts, the oxygen levels in Alberni Harbour have considerably improved since installation of the treatment facilities. The company, with the assistance of Fisheries Research Board staff, initiated in 1958 a weekly monitoring program in Alberni Harbour, particularly for dissolved oxygen (DO) (Waldichuk et al. 1969). This monitoring program continues and provides an early warning system on undesirable effects of the pulpmill effluent on the dissolved oxygen regime in Alberni Harbour. Dissolved oxyen concentrations at 9 metres depth (near bottom) continue to be low during May to August, sometimes dropping to zero in July (e.g., during 1981). But surface DO concentrations never appear to drop below 6 $mg \cdot L^{-1}$. The DO concentration at 3 metres is usually above 5 $mg \cdot L^{-1}$, but it did drop to 3.4 $mg \cdot L^{-1}$ in early June 1981 (unpublished data, MacMillan Bloedel Ltd.).

Work conducted in the early 1970s by Parker and associates (Parker and Sibert 1973; Sibert and Parker 1973) suggested that photosynthesis plays a major role in supplying oxygen in the Alberni Inlet system, and that the coloured pulpmill effluent inhibits penetration of solar radiation, and hence retards photosynthesis. They noted that the biological treatment of the effluent in the biobasin actually intensifies the colour and may be counterproductive in achieving the goal of improving the dissolved oxygen levels in Alberni Inlet. Their hypothesis has not been fully tested, and the significance of the colour of the effluent in comparison to the BOD in a situation such as Alberni Inlet has not been thoroughly investigated. Clearly, colour has more than just an aesthetic effect, but whether one could have alleviated the low dissolved oxygen problem in Alberni Inlet by merely removing the colour from the pulpmill effluent seems

rather dubious.

## 9. RESEARCH NEEDS

Even though the pressing needs for research on the biological effects of pulpmill effluents have diminished from the early days of the 1950s and 1960s, when new pulp mills were being installed and existing ones were being enlarged, and such marine living resources as oysters were being threatened, there remain many unsolved problems. New problems may be looming on the horizon. With the expected onslought of new and expanded mills in the next decade, there will undoubtedly be a renewed flurry of research on pulpmill pollution problems. The following "wish list" gives my perception of needed research on some of the problems that I regard as being of considerable importance.

### 9.1 Ecosystem Effect

In the long term, there is an aquatic ecosystem effect from disposal of pulpmill effluents which has not been fully quantified anywhere in British Columbia. There has been no long-term study in British Columbia on the effect of pulpmill effluents on any component of the ecosystem, such as there has been, for example, on the effect of deposition of pulpmill solids on the benthos in the Loch Linnhe - Loch Eil system in Scotland from the pulp mill in Fort William (Pearson 1975). Poole et al. (1977) have attempted to take a somewhat holistic approach in studying the effect of effluent from the pulp and paper industry on the estuarine ecosystem drawing on examples from the Canadian Atlantic Coast and Scotland. No microcosm studies have been conducted on the impact of pulpmill effluent on the ecosystem. There is a need for simple, routine measurements, possibly in some form of bioassay, e.g., on certain aquatic algae, that would provide an index of the effects of pulpmill effluents on freshwater and marine ecosystems.

### 9.2 Toxicity and Sublethal Responses

Biological assays on the acute toxicity of pulpmill effluents have been carried out routinely for many years (e.g., Alderdice and Brett 1957), and have provided a useful tool for waste management purposes. Somewhat arbitrary

application factors have been applied to the LC50 (concentration that is lethal to 50% of the test organisms over a given period of exposure) for effluents in order to provide a safety factor. In the past, the application factor has been usually arbitrarily chosen as 0.1, but in more recent time, an effort has been made to develop a scientific basis for such a safety factor, which has been equated to the sublethal threshold. Depending on approach used to measure the sublethal response, this factor can vary considerably (Walden 1976; Davis 1976).

There is a need for improving techniques for evaluating sublethal responses to pulpmill effluents not only of fish but also of commercially important invertebrates, e.g., oysters. There are practical needs for such information. For example, at what effluent concentration and temperature, does the swimming performance of adult sockeye salmon become impaired in freshwater? This may be of considerable importance in ascertaining whether migrating Fraser R. sockeye might be affected in reaching their distant spawning grounds in the Stuart Lake area. It is understood that even without the added stress of pulpmill effluent in the river water, some sockeye do not reach their spawning grounds and go unspawned during certain hot, dry summers. With respect to oysters, kraft mill effluent at sublethal concentrations appears to lead to a decline in condition factor (Quayle 1964) and flavour. What is the threshold effluent concentration for such a decline, and under what environmental conditions, does this effect begin to appear?

Behaviour response of fish and invertebrates to pulpmill effluents may be important from the point of view of management of certain species in the presence of such effluents. Speculation concerning the effect of the Gold River pulpmill effluent on migrations of adult coho and chinook (Tyee) salmon in Nootka Sound and Muchalat Inlet was noted earlier. While there have been some laboratory experiments on the avoidance response of fish to pulpmill effluents, more field studies of the type reported by Birtwell (1977) are needed.

### 9.3 Identification of Toxic Constituents and Determination of Their Ecological Significance

Biological assays on sulphite mill effluent (Williams et al. 1953) are based on the concentration of spent sulphite liquor related to the Pearl-Benson Index (Barnes et al. 1963). Bioassays on kraft mill effluent, however, are still

conducted utilizing the concentration of the total effluent being tested as the basis of concentration of toxicant (Walden 1976; Davis 1976). There is a need to be more specific in relating the toxicity in bioassays to some toxic constituent in the effluent.

Some work has been reported already on the isolation and chemical identification of toxic components in kraft mill wastes (Rogers 1973, 1976; Rogers et al. 1972, 1975; Leach and Thakore 1975). There are still numerous unidentified toxic constituents in kraft mill effluents, and no doubt research on the isolation and identification of some of these will be discussed at this Symposium. Such work should continue. Routine bioassays on fish and other aquatic organisms exposed to these substances must also continue. The significance of these waste materials in the aquatic ecosystem must be addressed as well, in addition to performing single-species bioassays.

### 9.4 Isolation and Quantification of Persistent Chlorinated Organics and Determination of Their Bioaccumulation by Aquatic Organisms at Various Trophic Levels.

Because assorted organic compounds are exposed to chlorination in the bleach plant, chlorinated organics are formed which tend to be quite refractory and persistent. The fate of most of these organochlorines is not known, and there is some concern that they may be bioaccumulated by certain aquatic organisms and biomagnified up the food chain to become a hazard for human consumers. More careful research of a rather sophisticated type with advanced techniques of extraction and instrumental identification is needed to solve some of the analytical problems. Once the substances are identified and their concentrations in chlorination effluents determined, there is a need to determine their behaviour and fate in the aquatic ecosystem and their effects on different species of aquatic organisms.

### 9.5 Treatment

There are numerous problems to be solved in connection with treatment of pulpmill effluents. As stated by Van Soest (1975): "The pulp and paper industry is an old industry, full of traditions, recipes, old-time operators and

suspicions..... The industry has also been most conservative in accepting new methods. Very few mills are prepared to be the first to try a new concept". In the effluent treatment field this certainly applies. Only tried and proven methods tend to be used. Some of the principal problems requiring research in effluent treatment that come to mind are as follows:

(1) Effectiveness of biobasins for reduction of toxicity of individual persistent constituents in the effluent. Biobasins appear to be operated as an art, very much dependent on the experience, skill and judgement of the operator, rather than as a bioengineering system. Parameters of efficient operation must be established so that handbook-type procedures can be developed.

(2) Improvements in ponding systems for reduction of BOD. The same arguments apply here as in the reduction of toxicity.

(3) Reduction in concentrations of wood solids in effluents by various techniques, and methods of recycling recovered wood.

(4) Foam separation of high-BOD and toxic constituents in kraft and bleach-plant effluents.

(5) Foam control using mill-generated substances such as green-liquor dregs.

(6) Elimination of such metals as cadmium from pulpmill wastes.

(7) Development of inexpensive and simple techniques for colour removal.

(8) In-plant control for producing a total effluent as near as possible to neutrality in pH.

## 9.6 Techniques of Effluent Disposal in Receiving Waters

There is a need for better understanding of the behaviour of pulpmill effluent in receiving waters and for development of techniques to achieve the most effective dilution and dispersion. It is undesirable to have accumulation of either the effluent or the wood solids, because of the impact such accumulations have on both water quality and on benthic habitats. Improved knowledge on effluent dispersal and on techniques that could most effectively achieve a high degree of dilution and dispersal in waters of British Columbia could be acquired by research on:

(1) Behaviour of effluent released from a submarine diffuser in both waters that are vertically mixed and vertically stratified.

(2) Development of improved techniques for tracing pulpmill effluent in the receiving environment.

(3) Design of diffusers to yield an effluent plume that can break through the pycnocline (layer where the density increases most rapidly with depth) but will not reach the surface in vertically-stratified coastal waters.

(4) Design of a diffuser system for riverine discharge of effluent that will prevent pockets of high concentration of effluent in the river and will allow effluent to be mixed rapidly into the river water.

(5) Determination of environmental effects of sub-surface, and particularly sub-pycnocline, pulpmill effluent fields on such water quality characteristics as dissolved oxygen in coastal waters.

### 9.7 Environmental Effects of a Shutdown of Pulpmill Production

The opportunity should be seized to study the effects of long-period shutdowns of pulpmills during the economic recession when markets for pulp and paper are down. For example, the rate of flushing of a particular body of receiving water can be determined if surveys are timed to precede and follow closure of a mill. The opportunity was taken to measure the rate of diffusion of effluent from the Prince Rupert pulpmill when it was shut down for summer maintenance in 1963 (Waldichuk 1966); and the distribution of kraft mill effluent in Alberni Harbour was easily mapped in the water that had cleared itself during mill closure, following the reopening of the mill after a labour strike in 1964 (Werner and Hyslop 1967). Even the effects of wood solids on recolonization of the bottom can be studied during long-term, or in some cases, permanent closure (e.g., Swanson Bay, Ocean Falls) of a pulp and paper mill (Fournier and Levings 1982).

## 10. CONCLUSIONS

The British Columbia pulp and paper industry is in the "doldrums" at present, figuratively speaking, owing to to the economic recession, and water pollution problems associated with the industry are no worse now than they were a decade ago. Water pollution has in fact been ameliorated somewhat by conversions of processes, e.g., calcium-base to the ammonia-base in the sulphite process, added in-plant controls and improved out-plant treatment and disposal facilities, such as biobasins and submarine diffusers. Only one sulphite mill (Port Alice) now remains in the province, the remainder having converted to kraft production. It

is expected that in the next decade the pulp and paper industry will rebound with a renewed effort to meet increased demands for paper products on the domestic and international markets. This may mean expansion of existing mills and even planning for new installations. New water pollution problems may emerge as a result of such expansion in the pulp and paper industry.

The trends in the last two decades have been toward construction of a greater proportion of new pulp and paper mills in the interior of the province as opposed to the coast, and adoption of the kraft chemical process rather than sulphite. This has meant a smaller per-ton pollution potential of the new mills but a greater impact of new installations in the pulp and paper industry on rivers than on coastal waters, although estuaries can also be affected by pulpmill effluents discharging into streams. A higher degree of treatment is generally required for interior pulp mills, which usually means clarifiers and/or settling basins for removal of wood solids and biobasins for reduction of BOD and toxicity. More rapid dilution and dispersion is provided for pulpmill effluent discharged into coastal waters, especially if this occurs in tide-swept channels, e.g. Discovery Passage, although severe pollution can arise in inlets that are not too rapidly flushed, such as Alberni and Neroutsos inlets. Ocean disposal, therefore, normally requires less stringent measures for pollution control; but most coastal mills have either installed or are in the process of installing clarifiers to remove wood solids, and submarine diffusers to achieve rapid dilution and dispersion, partly to satisfy the aesthetic aspects of coastal industrial waste discharges.

The main ecological problem associated with disposal of pulp and paper mill wastes continues to be low dissolved oxygen. This problem has arisen from effluent disposal at the sulphite mills at both Port Alice and Prince Rupert and with the kraft mill at Port Alberni. To solve the problem at the Port Alice mill, the sulphite process was converted from calcium bisulphite to a recoverable ammonium bisulphite base. At the Prince Rupert mill, the red liquor discharge from the original sulphite mill was first moved from the semi-enclosed Wainwright Basin to well-flushed Chatham Sound off the west side of Ridley Island. A kraft mill was added at Prince Rupert and the sulphite mill was subsequently closed down.

Acute toxicity has never led to massive fish kills in waters receiving effluents from British Columbia pulp and paper mills, although toxicity may have added to the stress from low dissolved oxygen. Sublethal effects undoubtedly occur and these may manifest themselves in various ways, including impairment of swimming performance, disruption of migration behaviour, interference with food searching and feeding, reduction in growth, and disruption of the predator-prey relationship. These sublethal effects, combined with other man-made and natural stresses, such as low flows and high temperatures in streams, could have an impact on stocks of salmon, inasmuch as some adult salmon might not be able to reach their spawning grounds and therefore die unspawned.

Recent problems that have arisen in the vicinity of coastal pulp mills relate to substances present in the sediments which are prohibited from being disposed of at sea, except in trace concentrations, under the Ocean Dumping Control Act. These include PCBs that were accidentally spilled into nearshore waters at the Prince Rupert mill and mercury that probably originated from the use of mercurial slimicides at most mills until about 1960. High cadmium levels, for which the origin is unknown, have created problems in disposal of dredge spoils from the Port Alberni and Powell River pulp mills.

Research needs continue on various aspects of the ecological effects of pulpmill effluents, including:
(1) effect on the total ecosystem; (2) sublethal effects on various aquatic organisms, such as the influence on swimming performance of adult salmon in freshwater and on condition factor of oysters in coasal waters; and (3) bioaccumulation of various organochlorines, formed by chlorination in bleach plants and present in pulpmill effluent, by aquatic species of commercial value. Problems of colour, foam, nutrients, odour, and microorganisms in pulpmill effluents have not been fully resolved, and research is needed to control undesirable conditions arising from these somewhat offensive characteristics of the effluents. There is a continuing need for research in process operations of pulp mills to minimize waste of wood products, process chemicals and water, and to increase the amount of recycling of chemicals and water and utilization of wood waste for energy within the plants. Bleachery wastes continue to be the most recalcitrant in treatment, and further research is needed to determine ways of rendering such wastes amenable to treatment or recycling, and therefore, less

harmful. Treatment of effluent has to be better based on careful scientific and engineering investigations to establish optimum conditions for the recovery of wood solids in settling lagoons and for the reduction of BOD and toxicity in biobasins, such as degradation of resin acids and chlorinated phenols.

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# THE POTENTIAL OF REMOTE SENSING FOR MONITORING PULP MILL EFFLUENTS

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## 1.0 INTRODUCTION

In 1858, Gaspard Felix Tournachon ascended several hundred meters in a balloon over Paris to take the earliest reported aerial photographs. Today, one hundred and twenty-five years later, remote sensing has evolved into a complex and varied discipline in which information about our environment is acquired from a variety of airborne, spaceborne and ground-based platforms.

Remote sensing employs cameras and a number of other sensing devices which measure and record electromagnetic energy that has been reflected or emitted from the surface or atmosphere of the earth. Sensors are available to measure a wide range of the spectrum from the very short wavelengths at which gamma rays are emitted to the compartively long wavelengths at which radar operates. Judicious usage of these sensors can secure far more information about an area than can be obtained with conventional photography, which is limited to the visible light portion of the spectrum.

Aerial remote sensing offers two particular advantages over ground-based (or water-based) field measurements of effluent quality. Firstly, it offers improved coverage of the scene by viewing the complete area almost at once; and secondly remote sensing techniques can be highly cost and time effective when compared with conventional sampling methods.

By common usage, effluents are considered liquid in nature. However, "Waste material (as smoke...) discharged into the environment" can also be defined as an effluent (Webster, 1981). This paper reviews the remote sensing options available for monitoring pulp and kraft mill effluents, in both gaseous and liquid form. The paper also includes a

brief description of a novel airborne platform under development by B.C. Research and its possible application to pulpmill effluent monitoring.

## 2.0 SENSOR OPERATIONS

There are a wide variety of airborne and satellite sensors available for the assessment of such water quality parameters as suspended sediments, water colour, temperature, chlorophylls and dissolved organic materials. Each combination of sensor and platform offers unique qualities which must be assessed in respect to their suitability to the task in hand and their cost effectiveness. Brief descriptions of several sensors citing their advantages and limitations for water quality studies appear below. Additionally, new technology available for the monitoring of gaseous emissions is reviewed.

### 2.1 Aerial Photography

Aerial photography can take many forms due to the wide variety of camera formats, platforms and film emulsions that are availble. Cameras range from 35 mm amateur equipment to large format (225 mm) cameras. Aircraft used vary in size from small, single-engine piston-powered craft operating at low altitudes, to multi-engine jet aircraft for medium and high altitude photography. Tethered balloons and helicopters are also employed as aerial platforms for photography. Monochrome and colour film emulsions are used to record reflected energy in the ultra-violet, visible, and near-infrared portions of the spectrum. Aerial photography offers the lease expensive airborne sensing option for many needs and is the data source most readily accepted by non-specialists.

Aerial photography can provide data for both qualitative and quantitative analysis of effluent discharges. Visual interpretation of black and white, natural colour, and false-colour infrared photography can be used for the detection and mapping of colour anomalies and suspended

sediment concentrations. Tracer dyes may be used to enhance the visibility of mill discharges to aid interpretation. Analogue enhancement techniques, such as the division of image grey levels into a number of discrete, colour-coded intensities (density slicing) may also be applied to photographic data to improve its interpretability.

Visual interpretation of aerial photography can further be used to assess the effects of effluent discharges on the environment of the outfall area. Through the detection of vegetation damage and bedrock discolouration from airborne effluents, and the detection of shoreline vegetation damage, water discolouration, algal blooms or excessive sedimentation for water-borne effluents, useful information to assist in the assessment of outfall behaviour may be gained. The synoptic view acquired from the aerial perspective provides a unique tool for recognizing an outfall pattern and its environmental effects.

Quantitative analysis of photographic data can be undertaken by extracting densitometer readings from the film emulsion, and relating these to field data acquired simultaneously with the photography. The qualities of film exposure, film density and scene reflectance for the particular image must be accounted for when establishing the relationship between density measurements and the field data, making this process quite complex and exacting. Densitometer data extracted from colour and colour-infrared photography has been used quantitatively to estimate suspended solid concentrations throughout the mixing zone at a pulp mill in Wisconsin (Klooster and Scherz 1974, Lillesand 1975).

## 2.2 Airborne Multispectral Scanner

The multispectral scanner (MSS) is an optical-electronic device capable of recording reflected energy in up to eleven discrete wavebands simultaneously. Detectors can sense radiation in the ultra-violet, visible, near-infrared and middle infrared portions of the spectrum. These data are recorded on magnetic tape in digital format for subsequent

computer analysis. "Quick-look" photographic images may also be processed for each channel of data, although these products are of little analytical value.

MSS data provide the advantages of improved spectral range and spectral resolution when compared with aerial photography. MSS data offer flexibility in the choice of waveband or waveband combinations to be analysed, and the digital data are readily amendable to computer processing and enhancement. The ground resolution of this sensor is determined by the altitude of the aircraft and generally ranges from approximately 3 m to 20 m.

As with aerial photography, MSS data can be analysed both qualitatively and quantitatively. Visual interpretation of computer enhanced photographic MSS products can be beneficial to the same applications as aerial photography. Quantititave analysis may be undertaken in a method similar to that for aerial photography if relationships between digital MSS values and field data are established.

Some disadvantages associated with MSS data include the limited availability of scanners, the high costs of data acquisition, inherent distortions resulting from scanning geometry, and the requirement for digital analysis facilities. An airborne MSS mission in British Columbia is likely to cost several tens of thousands of dollars. Digital image analysis services cost in the order of $100/hr and are not widely available in Canada.

## 2.3 Thermal Infrared Line Scanner

This aerial sensing device is uniquely suited to the detection of thermal plumes and mixing patterns of mill effluent. Detecting emitted radiation in the 8-14 um band, this sensor is capable of detecting surface temperature differences of 0.5°C (Lillesand and Kiefer 1979). Internal calibration of the sensor provides quantitative data without the requirement for ground truth. The scanner provides either photographic or digital data which may be analysed by visual or computer methods.

Additionally, analogue "density slicing" (Section 2.1) techniques may be applied to the photographic data. The disadvantages associated with these data are similar to those of the MSS. The high cost of data acquisition is perhaps the most significant.

## 2.4 Laser Fluorosensor

The laser fluorosensor is an optical-electronic profiling sensor (non-imaging) that employs a laser to excite surface materials such that they emit radiation by fluorescence. An ultra-violet induced fluorescense in the visible blue wavelengths (0.406 um) has been found to correlate with concentrations of dissolved organic material (lignin sulphates) in pulp mill effluent (Bristow, 1978). This makes the laser fluorosensor a useful tool for the detection of the boundaries of a discharge plume containing dissolved organics and to profile concentrations of these compounds within the plume. The availability of field data would allow calibration of this device for quantitative analysis.

As a non-imaging device, this sensor has restricted application in monitoring mill effluents. One advantage cited for the use of remote sensing was its ability to provide a synoptic view of a discharge area. Clearly, this sensor does not offer this advantage. Moreover, such devices are not used routinely and their availability is limited. The cost for a laser fluorosensing mission in British Columbia would be similar to that of an airborne MSS overflight.

## 2.5 Satellite Remote Sensing

There are several satellites now orbiting the earth which provide image data from the remote sensing of both land and water surface features. All provide a synoptic overview; only one is considered to be of potential application in pulp mill outfall studies. The LANDSAT series of satellites have been orbiting the earth since 1972 providing continuous images of surface conditions.

In July 1982, the most recent Landsat satellite (LANDSAT-4) was launched, carrying a new sensor called the Thematic Mapper (TM). The TM is a spaceborne multispectral scanner similar to the MSS described in Section 2.2. The TM records electromagnetic energy in seven spectral bands in the visible and infrared portions of spectrum at a ground resolution of 30 m. A new TM image of an area is acquired every 16 days providing multitemporal monitoring capabilities. TM data will be widely available in 1984. The cost for photographic images of TM data will be in the order of tens of dollars, whilst computer tapes containing digital image data will cost several hundreds of dollars.

The 30 metre ground resolution of the TM does not provide for a detailed survey of small areas, but is sufficient to provide a "general" mapping capability. A very important characteristic of these data is that TM images from different dates can easily be overlaid to detect changes.

In pulp and kraft mill applications, data from this satellite are likely to be of most value in monitoring the effects of effluent discharges on the neighbouring environment. Since scene reflectance characteristics for a given satellite image can be readily computed, the satellite data can provide quantitative information with minimal field data.

A second application for these data may be for the quanititative mapping of surface suspended sediment concentrations. Alfoldi and Munday (1977) have shown that data from earlier Landsat satellites can be used to map sediment concentrations in coastal environments. Improvements in the spatial resolution and spectral range of the TM may allow sediment mapping over much smaller bodies of water, and at improved accuracy.

## 2.6 Gaseous Effluent Monitoring

Kraft pulp mills have many points of discharge to the atmosphere. Continuously monitoring the composition and the flow rate of each of these discharges is a difficult and expensive undertaking. Therefore, it is common to monitor only the composition of major

discharges - the recovery furnace stacks for odorous sulphur gases, and the power boiler stacks from opacity or particulate loadings. The development of remote sensing instruments makes it feasible to monitor the total discharge being emitted from a mill. Plume velocity can be determined using laser-Doppler velocimetry. Gas and particulate concentrations can be remotely determined using tunable dye lasers for differential absorption lidar (light detection and ranging). This technique (DIAL) results in a two dimensional map of the pollutant species concentration profile which, when combined with the velocimetry data, yields the mill's total emission rate for that given species.

Atmospheric reactions and plume dispersion can be followed using DIAL or by means of remote Fourier transform infrared (FT-IR) spectroscopy. At present these tools are being used to identify and quantify short-lived intermediate species in photochemical smog production - they could also be used to follow the oxidation of the various reduced sulphur species emitted from a kraft pulp mill.

The present use of these sensors is limited by availability and cost. As the price of hardware decreases, it can be expected that DIAL and remote FT-IR will in future mature into cost effective systems for monitoring the emission of pollutants from pulp mills and to determine the fate of these emissions in a given air-shed.

## 3.0 CONCLUSIONS

From the above review, it is clear that remote sensing technology offers many desirable capabilities useful for pulp mill effluent monitoring. However, the cost effectiveness of employing certain of these techniques in an operational environment can be legitimately questioned. The remote sensing option which has proved itself in operational water quality monitoring is aerial photography (California State Water Resources Control Board 1978).

The use of small format (35 mm or 70 mm) photography acquired from light aircraft offers the least expensive means of acquiring such data for effluent detection and mapping. In concert with field investigations, quantitative information on suspended sediment concentrations may be extracted from these data.

With its superior spectral and spatial resolution over previous satellites, it is expected that the LANDSAT-4 TM will provide a timely, inexpensive and widely available source of data for environmental monitoring. The successful application of these data to monitoring large effluent discharges and their effect on the outfall environment is anticipated in light of work undertaken with previous LANDSAT data.

## 4.0 B.C. RESEARCH REMOTELY PILOTED AIRCRAFT

In 1982, B.C. Research began to study the feasibility of using small, remotely piloted aircraft (RPA) as platforms for aerial photography. Advantages associated with these aircraft include low cost (capital and operating), ease of operation, portability, safety and very low speed, low altitude capability. Using a 3-meter wingspan aircraft, B.C. Research has demonstrated the value of these systems in such applications as pollution surveys, wildlife inventories, site mapping and marine ecology (Tomlins and Monroe, 1983). A new general purpose RPA is now under development to be operational in 1983 (Tomlins, 1983). This aircraft will carry two 35 mm camera systems and a black-and-white video camera. An avionics package has been developed to control aircraft altitude and attitude. Video signals will be transmitted in real time to a ground monitor and used to navigate the aircraft. Photography may be acquired in black-and-white, colour and/or colour infrared according to mission requirements. The feasibility of equipping the aircraft with a payload for atmospheric sampling is currently being investigated.

The aircraft is ideally suited to surveillance of small study sites (rivers, small outfall areas) and is an effective and cost efficient means of acquiring aerial data in effluent studies.

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# DIFFUSER DESIGN AT THE POWELL RIVER PULP MILL

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## ABSTRACT

This paper summarizes some of the basic theory and field data used in the design of the outfall and diffuser system of the Powell River Division of MacMillan Bloedel Limited.

A summary is also made of the effluent dye tracer study of the Powell River Diffuser.

We wish to thank Mr. A. Chmelauskas, MacMillan Bloedel Limited, for making the extensive diffuser performance study of Dobrocky Seatech available to us. Based on the data obtained, under worst case conditions, the effluent diffuser is capable of achieving dilutions 200:1 within the initial dilution zone of 100 m from the diffuser centreline.

The assistance of Mr. N.H. Dinsmore, H.A. Simons (International) Ltd. is gratefully acknowledged.

## DESIGN PARAMETERS

1. The effluent disposal system is to handle a combined acid and alkaline normal flow of 18,000 USGPM.

2. The dilution requirements for the diffuser were to be based on anticipated mill effluent toxicity given by a 96 hour LC50 of 10%.

3. To meet the requirements for maximum effluent concentrations of 0.05 toxic units within the initial dilution zone (300 ft. radius from the diffuser) an average dilution of 200:1 would be required.

ENGINEERING ANALYSIS

Dilutions Required because of Toxicity

Dilutions required to reduce KME toxicity to acceptable levels is based on studies done by Dr. J. C. Davis.

$$\text{Toxic Units} = \frac{\text{Concentration of Toxicant Present in Solution}}{\text{Concentration of Toxicant Equivalent to 96 hr. } LC_{50}}$$

where concentration is expressed as a decimal fraction:

Toxic Units = 0.05 maximum

$$\text{Required Dilution} = \frac{1}{0.05 \times \text{96 hr. } LC_{50}}$$

At 40 cfs mill effluent flow and a $LC_{50}$ of 10% then the average dilution required for 0.05 toxic units is 200 at 300 ft. from the diffuser.

Diffuser Analysis

Because of very high initial dilution requirement of 200:1, we had to use alternate methods of analysis as a check. This 200:1 is double that required on most of the major operating outfalls.

In the following analysis the spacing of the discharge ports is large enough to prevent merging of plumes based on water depth. Average dilution equals twice minimum dilution, $S_M$.

Analysis

Consider the wastewater field one third water depth.

Consider the width of the field to be length of diffuser plus water depth over the diffuser.

For design purposes, the current velocity used to assess dilution, is the mean of the net current velocities at 35 ft and 125 ft:

$$U_A = \frac{0.17 + 0.06}{2} = 0.12 \text{ fps}$$

$$\frac{(L + H)(0.3H)(0.12)}{40} = 200$$

$$\frac{(L + H)(0.3H)(U_A)}{Q_T} = \text{Dil.}$$

$$U_A = Q_T \text{ . Dis.}/(L + H)(0.3H)$$

where L = Diffuser length, ft.

H = Water depth, ft. (200 ft. conservative depth)

$Q_T$ = Total discharge, cfs

Dil. = Dilution

$U_A$ = Ambient current, fps

Based on the oceanographic data, the minimum net ambient current expected across the diffuser section will be equal to or greater than 0.12 ft./sec.

Critical period of time is defined when equation "A" is not satisfied.

Consider the volume of water storing the effluent above the vertical discharge ports is given by the following:

$$V_S = 10(0.65H)^2(L + 0.65H)$$

where $V_S$ = Volume of water storing effluent, $ft.^3$

H = Water depth

L = Diffuser length

Field tests have indicated with a vertical discharge in the ocean, the vortex created will move 5 to 8 times the vertical distance, upstream and downstream of the diffuser. We have considered the vertical travel to be 0.65 x the water depth.

If we consider a 2 hour slack period when the ambient current is less than needed to provide the dilution requirement and during this time we consider the ambient current to be zero:

$$L = \left(\left(\frac{\text{Dil.} \times Q_T \times \alpha \times 2 \times 3600}{(4.23H^2)}\right) - 0.65H\right)$$

where Dil. = Average dilution

$Q_T$ = Mill discharge, cfs

$\alpha$ = Concentration variation in storage volume

H = Water depth, ft.

L = Diffuser length, ft.

Diffuser length for 40 cfs, 225 ft. water depth, 2 hour slack period variable concentration variation:

| Q cfs | Dil. | $\alpha$ | H ft. | L ft. |
|---|---|---|---|---|
| 40 | 200 | 5 | 225 | 1200 |
| | | 4 | " | 930 |
| | | 3 | " | 660 |
| | | 2 | " | 390 |

We use a diffuser length of 1,080 ft. considering $\alpha$ equal to 4, which appears to be confirmed from the dye studies.

REVEIW OF EFFLUENT DYE TRACE STUDY OF THE POWELL RIVER DIFFUSER

Oceanographic Operational Study

The following gives a resume of conditions and methods for the Dobrocky Seatech Limited study over the perio. February 27 to March 1, 1981.

Study

a. Period of slack tide currents.
b. Thin surface freshwater layer overlying a salt water layer having little density stratification.
c. Study under oceanographic conditions which would create a "worst case" test of the diffuser's performance.
d. Rhodamine WT dye was injected into upstream of the outfall to be certain of complete mixing with effluent.
e. Variosens In Situ Fluorometer
This a very sensitive fluorometer which is capable of measuring variations in the concentration of Rhodamine WT dye over four orders of magnitude without any scale changes being required.

Figure

1 Shows the location of the study area.
2 Location of vertical profiles taken on March 1, 1981.
3-4 Variosens profiles.
5 Profile transect along diffuser.
6 Dye dilution contours.

The diffuser performance was tested against design specifications which were intended to produce an effluent dilution of 200:1 within the initial dilution zone defined as being 100 m from the diffuser.

The diffuser system has 36 ports spaced on 45 ft. centres but during the test, 12 of the inshore ports were capped. The extra ports were added to provide more hydraulic capacity in the outfall and diffuser system and also provide flexibility in modifying the diffuser length, if the field test did show the required dilution was not reached in the initial dilution zone. The low water depths over the open ports range from 61-76 meters (200-250 ft.).

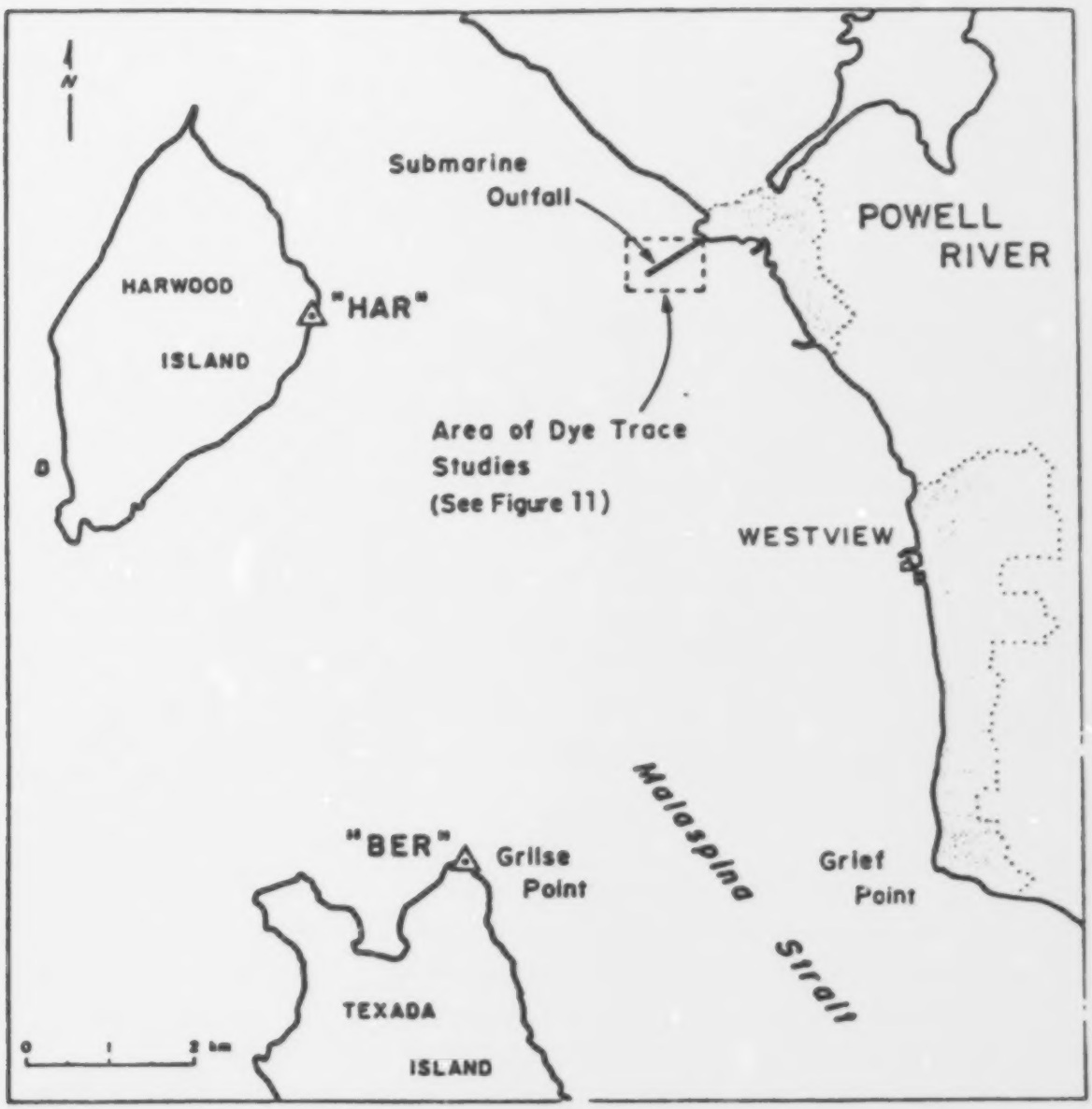


FIGURE 1 LOCATION OF STUDY AREA SHOWING AREA OF DYE TRACER STUDY AROUND OUTFALL AND POSITIONING SHORE STATIONS ("HAR", "BER").

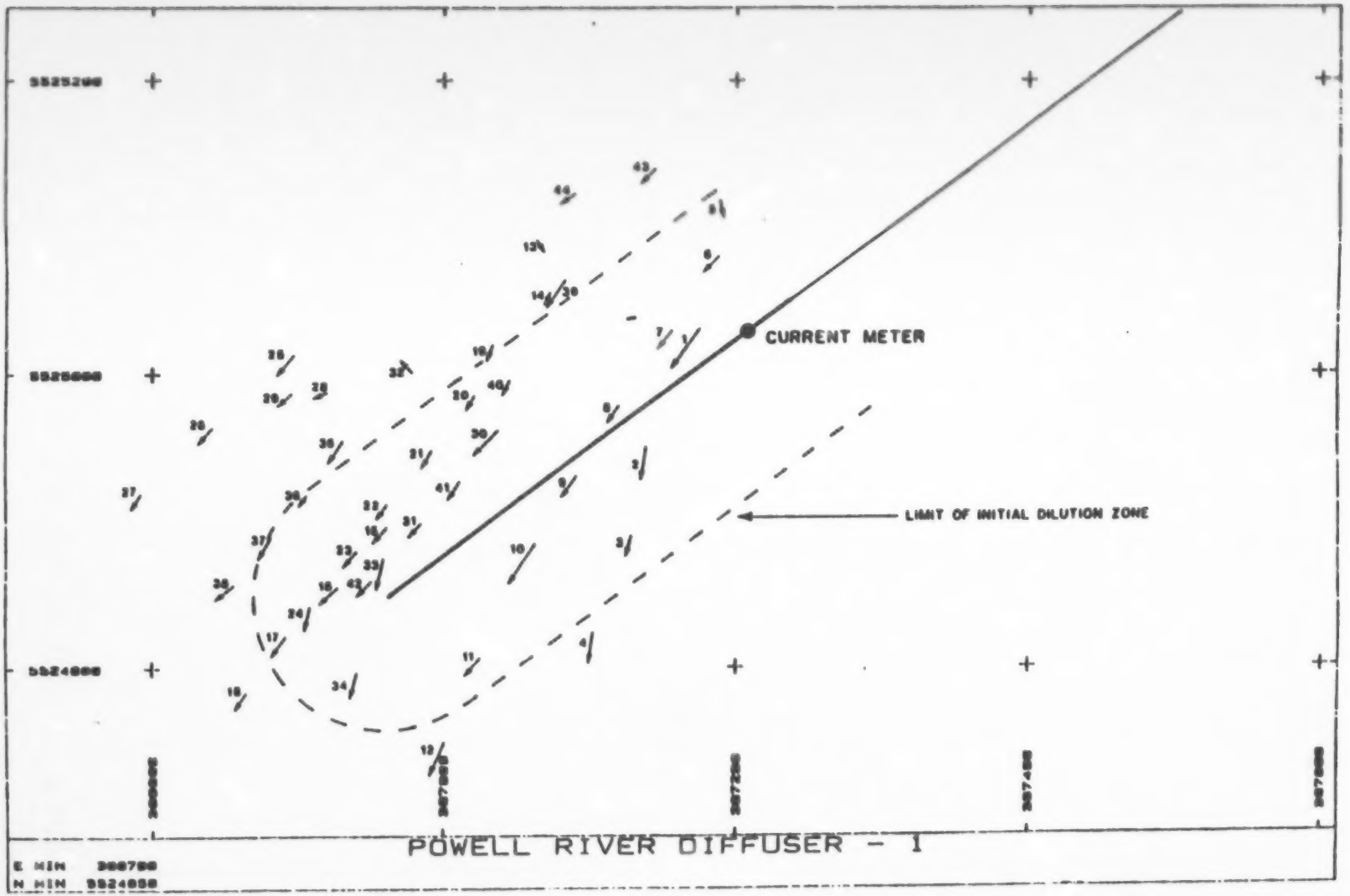


FIGURE 2 LOCATION OF VERTICAL PROFILES TAKEN ON MARCH 1, 1981.
ACTIVE LENGTH OF DIFFUSER IS SHOWN AS WIDER LINE.

Dilution Factor (X:1)

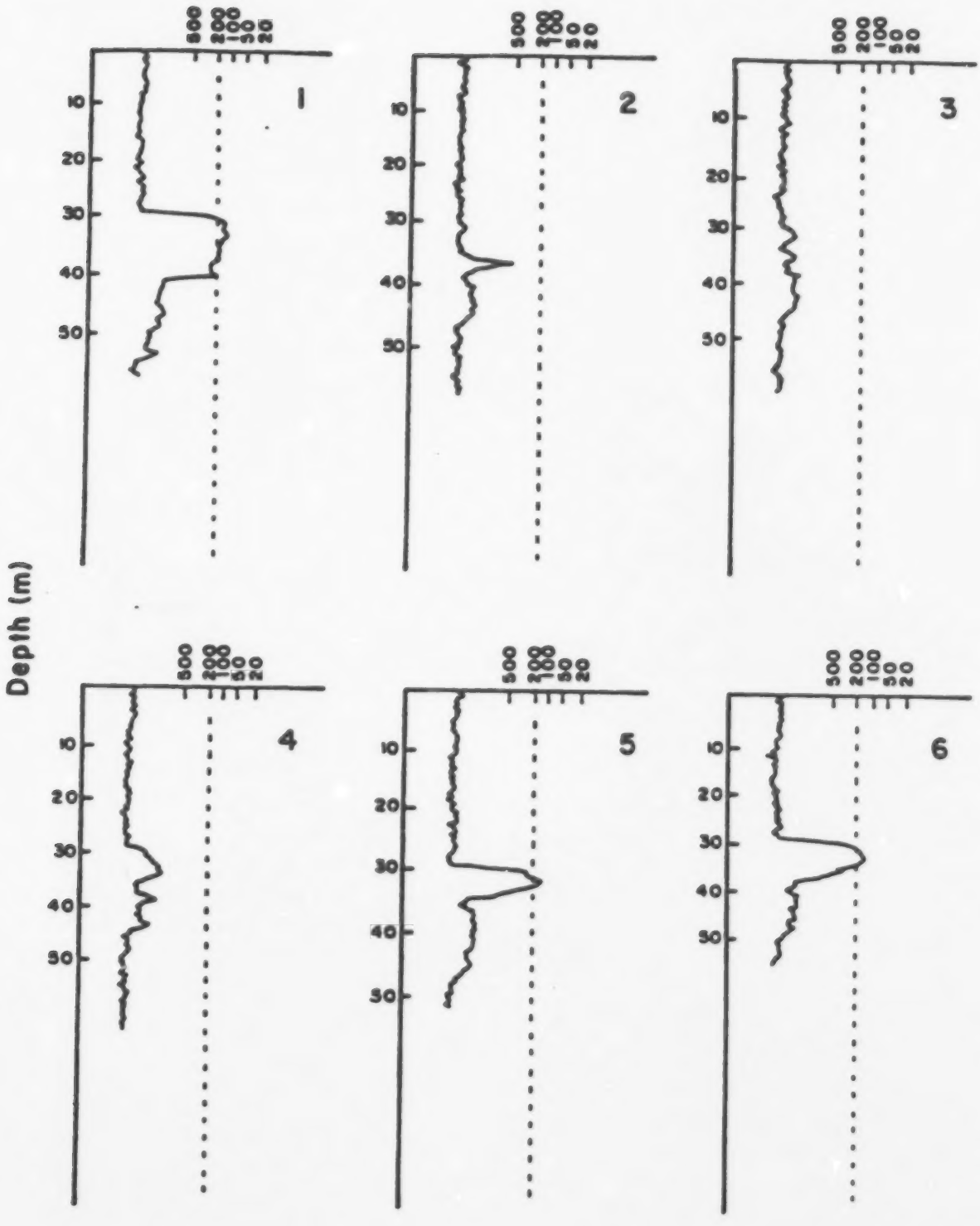


FIGURE 3 VARIOSENS PROFILES 1 - 6

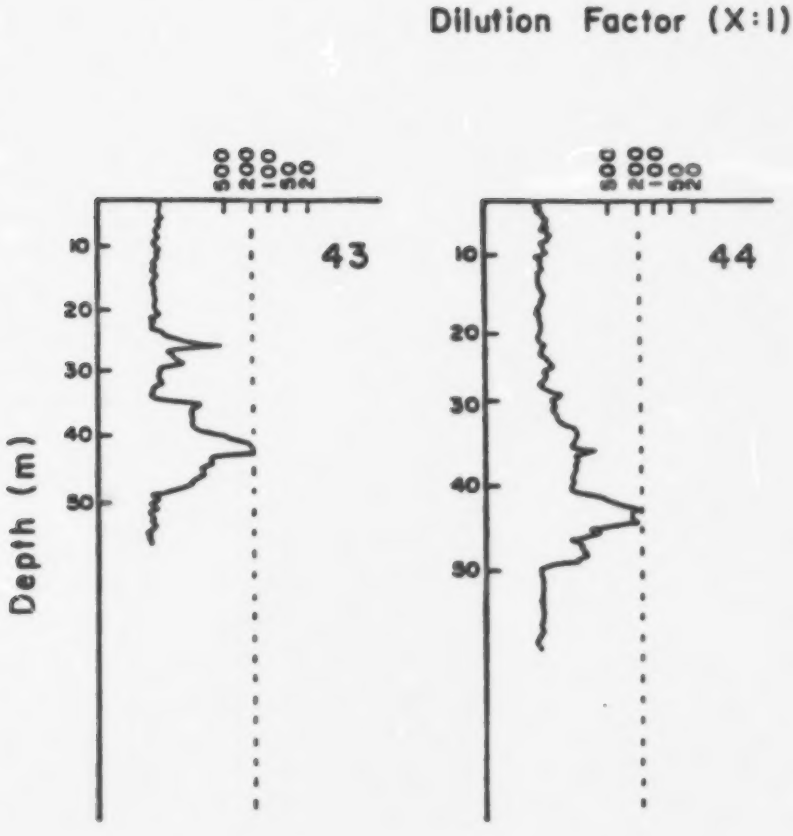


FIGURE 4 VARIOSENS PROFILES 43 - 44

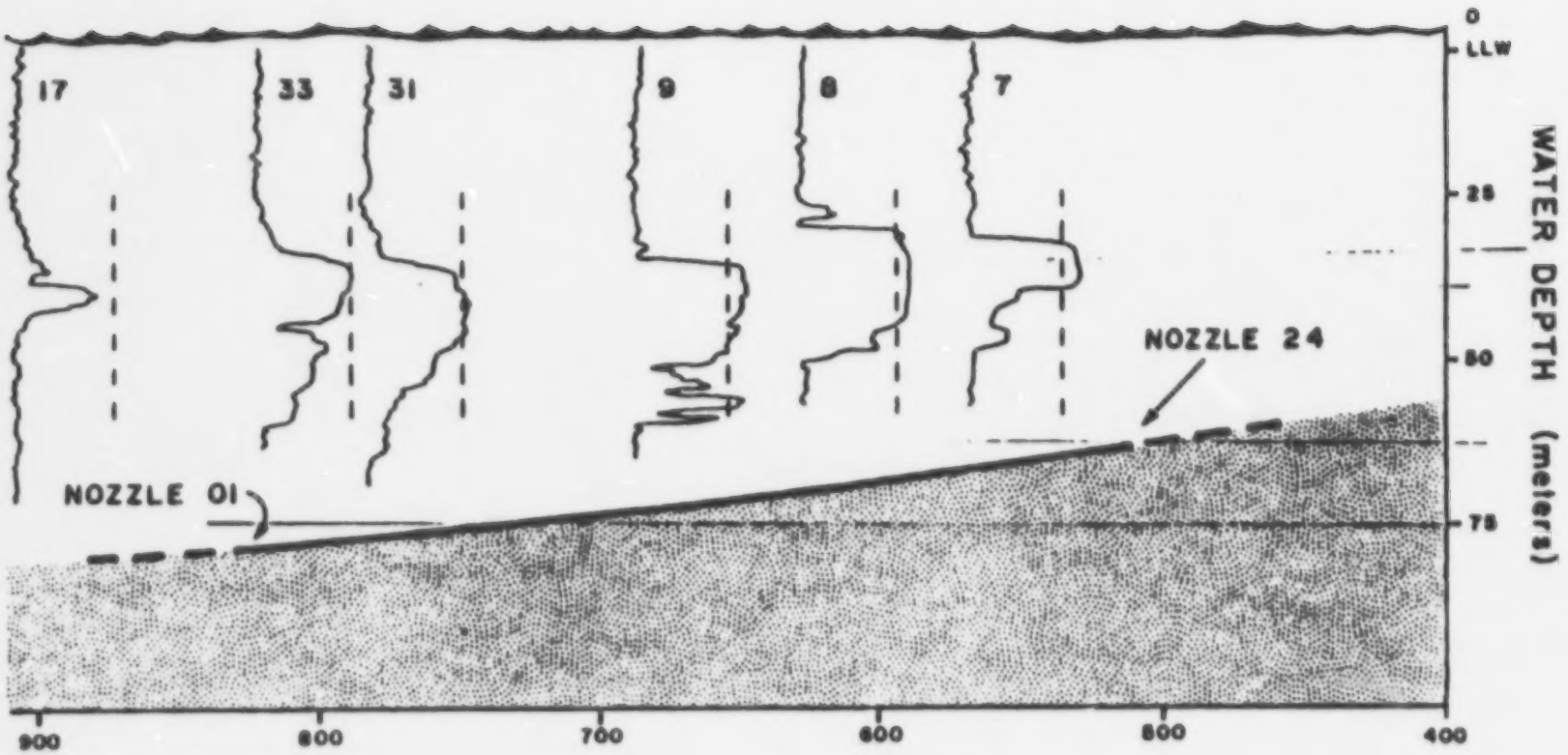


FIGURE 5 PROFILE TRANSECT ALONG DIFFUSER SHOWING ACTIVE LENGTH BETWEEN NOZZLES 01 - 24. THE VERTICAL DASHED LINES FOR EACH PROFILE CORRESPONDS TO THE 200:1 DILUTION LEVEL.

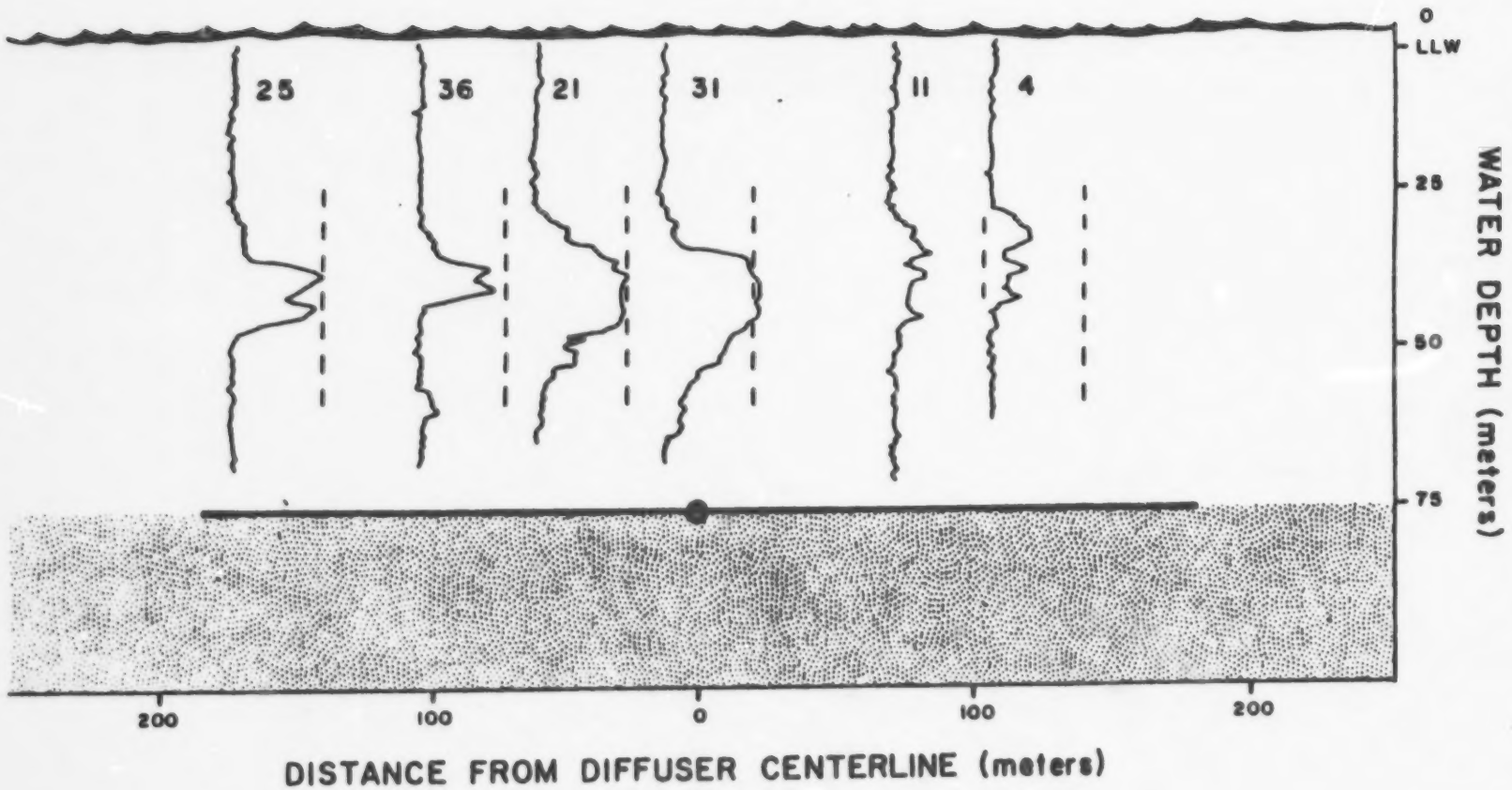


FIGURE 6 PROFILE TRANSECT ACROSS DIFFUSER. VERTICAL DASHED LINES FOR EACH PROFILE CORRESPONDS TO THE 200:1 DILUTION LEVEL.

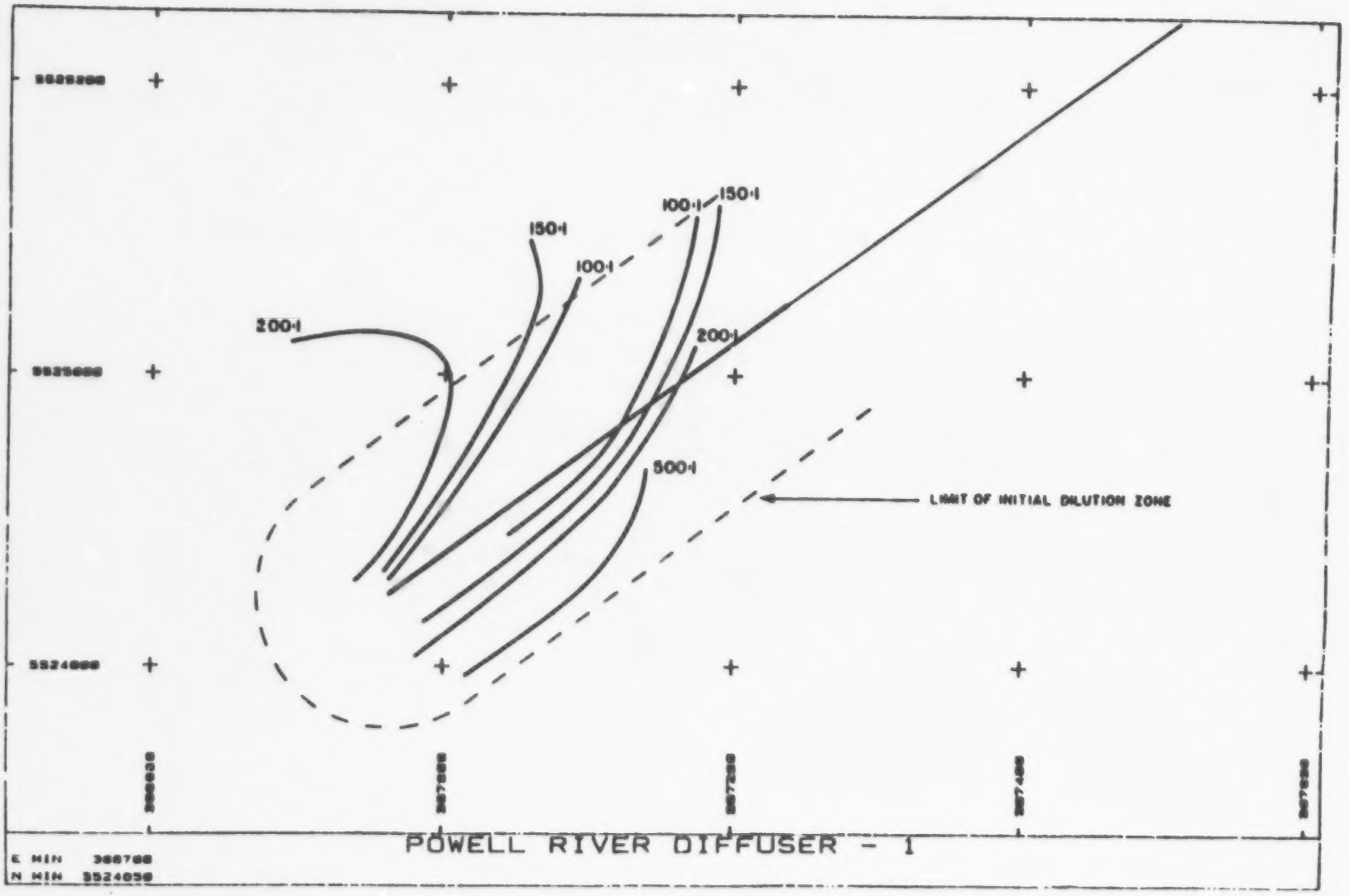


FIGURE 7 DYE DILUTION CONTOURS FOR MARCH 1, 1981.

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APPENDIX A

Alternate Methods of Analysis in the Design of the Powell River Diffuser

Powell River. Calculation of average dilution using analysis which gave best agreement for Harmac test.

Plumes in a stagnant environment:

$$S_a = 0.46\, Q^{-\frac{1}{2}}\, \Delta o^{\frac{3}{4}} (dp/dz)^{-5/8}$$
$$= 0.46(0.04)^{-\frac{1}{2}}(25^{\frac{3}{4}})(0.0185^{-5/8} = 139$$
$$\Delta h = 4.6(0.04 \times 25)^{\frac{1}{4}}(0.0185)^{-3/8} = 20.5 \text{ m}$$

Using the net current speed of 2.2 cm./sec.:

$$U > 0.0036(25 \times 0.04)^{\frac{1}{4}}(0.0185)^{1/8} > 0.002 \text{ m/s}$$
$$S_a = 3.0\left(\frac{0.002}{0.04}\right)^{1/3}(25/0.0185)^{2/3} = 300$$

The density profiles for the diffuser area were drawn up from U.B.C. Institute of Oceanography data, for 1972 and 1973 and from Dobrocky Seatech Limited's measurements of October 4, 1976.

The greatest variation in densities of the water column occur in the top 70 ft. of depth.

Density Profiles from Dobrocky Seatech Study

$\frac{dp}{dz} = 0.009$

$\Delta o = 25$

$Q = 0.04 \text{ m}^3/\text{s}$

$S_a = 0.46(0.04)^{-\frac{1}{2}} 25^{\frac{3}{4}}(0.009)^{-5/8}$

$= 218$

$\Delta h = 4.6(25 \times 0.04)^{\frac{1}{4}}(0.009)^{-3/8}$

$= 27 \text{ m}$

We use the net current of 2.2 cm./sec. at 35 m depth.

Plumes in a flowing environment:

$$S_a = 3.0\left(\frac{U}{Q}\right)^{1/3}(\Delta o/(dp/dz))^{2/3}$$

$$\Delta h = 2.3(\Delta o\ Q/(U \times dp/dz))^{1/3}$$

$$S_a = 3.0(0.022/0.04)^{1/3}(25/0.009)^{2/3}$$

$$= 486$$

U = Ambient current, m/s

$\Delta h$ = 40 m

The average dilution is greater than that given by the earlier density profiles and still exceeds the required 200:1.

Equation applicable when:

$$U > 0.0036(\Delta\ o\ Q)^{\frac{1}{3}}(dp/dz)^{1/8}$$

$$U > 0.00199$$

Let us consider dp/dz = 0.018

$$0.0036(25 \times 0.04)^{\frac{1}{3}}(0.018)^{1/8} = 0.00218$$

$$S_a = 3.0\left(\frac{0.022}{0.04}\right)^{1/3}(25/0.018)^{2/3} = 306$$

$$\Delta h = 2.3(25 \times 0.04)/0.022 \times 0.018))^{1/3} = 31 \text{ m}$$

Dilution is still acceptable when tested for greater density gradient.

Let us use the following equation as an alternate analysis:

$$S_m = 0.16\ Y\ (W/L)^{-2/3}$$

where $S_m$ = Minimum dilution
$Y$ = Vertical travel of plume, m
$Q$ = Total diffuser discharge, $m^3/s$
$L$ = Diffuser lenght, m

$$S_m = 0.16 \times 31 \times \left(\frac{35}{3.281^2 \times 1000}\right)^{-2/3} = 226$$

Average Dilution = 452

Dilution will be acceptable for the proposed diffuser length of 1,000 ft.

$$S_m = \alpha(0.065H)(Q/L)^{-2/3}$$

where $S_m$ = Minimum plume dilution
$H$ = Water depth, ft.
$Q$ = Total diffuser discharge, cfs
$L$ = Diffuser length, ft.

We assume vertical travel is 65% of water depth.

To find value of $\alpha$ using Harmac test results, Harmac water depth over diffuser:

325 - 300 ft.

$$\alpha = (S_m/(0.65H \times (Q/L)^{-2/3}))$$
$$= (100/(0.65 \times 312 \times (102/625)^{-2/3}))$$
$$= 0.15$$

To check diffuser length at Powell River using the Powell River water depth over diffuser:

250 - 200 ft.

$$L_{ft.} = (Q_{cfs} \times \left(\frac{S_m}{0.15 \times 0.65H}\right)^{3/2})$$

$$= (40 \times \left(\frac{200}{0.15 \times 0.65 \times 225}\right)^{3/2})$$

$$L = 1{,}100 \text{ ft.}$$

During the Powell River diffuser study, the following conditions existed:

1. Mill flow 35 cu.ft./sec.
2. 24 diffuser ports open.
3. Operating diffuser length, 1,035 ft.
4. Average water depth over diffuser, 225 ft.

$$S_m = 0.15(0.65 \times 225)\left(\frac{35}{1035}\right)^{-2/3}$$

$$= 210$$

The Powell River diffuser has 36 ports on 45 ft. centres, thus when all ports are open, the effective diffuser length is 1,575 ft. During the test only the furthest 24 ports from shore were operating.

The following table summarizes the Harmac and Powell River test data.

DIFFUSER TEST DATA

| | No. of Ports | Port Vel. ft./sec. | Equiv. Port Dia., ft. | Froude No. | $S_m$ |
|---|---|---|---|---|---|
| Harmac | 4 | 11.7 | 1.67 | 10 | 100-200 |
| Powell | 24 | 7.5 | 0.50 | 12 | > 200 |

Another equation has been used to define minimum dilution $S_m$ with Foude number, vertical travel of plume and diameter of discharge port.

Using Harmac test data:

$$S_m = \beta (F_r^{-2/3})(Y/Dj)^{5/3}$$

$$\beta = (S_m(F_r^{2/3})(Y/Dj)^{-5/3})$$

$$= 0.16$$

$$S_m = 0.16\ F_r^{-2/3}(Y/Dj)^{5/3}$$

As a consecutive analysis for Powell River we use $F_r = 15$.

Powell River

$$Y = 0.65H$$

where H = water depth over diffuser

$$S_m = 0.16(15^{-2/3})\left(\frac{0.65(225)}{0.50}\right)^{5/3}$$

$$= 339$$

Let us consider the average dilutions using Variosens profiles of Dobrocky Seatech Limited at profiles 1, 8, 9, 33, 5, 39, 19, 35, 36, 37, 17, 34, 11 and 4.

AVERAGE DILUTIONS

| Profile | Average Dilution |
|---|---|
| 1 | 600 |
| 8 | 500 |
| 9 | 450 |
| 33 | 500 |
| 5 | 600 |
| 39 | 600 |
| 19 | 600 |
| 35 | 600 |
| 36 | 600 |
| 37 | 650 |
| 17 | 600 |
| 34 | 600 |
| 11 | 650 |
| 4 | 650 |

APPENDIX B

## Design of Powell River Outfall and Diffuser System

Outfall and Diffuser Design. The following table gives the diameter of discharge ports starting at the end port furthest from shore. The discharge ports are vertical with a spacing of 45 ft.

| Port No. | Port Dia. in. | Diffuser Dia. in. | Port No. | Port Dia. in. | Diffuser Dia. in. |
|---|---|---|---|---|---|
| 1 | 10.25 | 24 | 13 | 6.125 | 36 |
| 2 | 9.75 | 24 | 14 | 6.00 | 36 |
| 3 | 9.00 | 24 | 15 | 5.875 | 36 |
| 4 | 8.50 | 24 | 16 | 5.75 | 36 |
| 5 | 8.00 | 24 | 17 | 5.75 | 36 |
| 6 | 7.625 | 24 | 18 | 5.625 | 36 |
| 7 | 7.375 | 30 | 19 | 5.500 | 42 |
| 8 | 7.125 | 30 | 20 | 5.438 | 42 |
| 9 | 6.875 | 30 | 21 | 5.375 | 42 |
| 10 | 6.625 | 30 | 22 | 5.250 | 42 |
| 11 | 6.50 | 30 | 23 | 5.250 | 42 |
| 12 | 6.25 | 36 | 24 | 5.187 | 42 |

$$\frac{\text{Nozzle Area}}{\text{Diffuser Area}} = \frac{(1130)}{42^2}$$

$$= 0.64$$

The following gives the average plume dilution generated by the outplume computer model by Teeter and Baumgartner:

Powell River

TRAPPING DEPTH, DILUTIONS FOR VARIOUS PORT DIAMETERS
DEPTH OF FLOW AND VERTICAL PORT VELOCITIES

| Port Dia. m | Ambient Current m/s | Disch. Depth m | Port Vel. m/s | Trapping Depth m | Dilution |
|---|---|---|---|---|---|
| 0.250 | 0.022 | 70 | 1.46 | 34 | 300 |
| 0.150 | 0.022 | 60 | 4 | 30 | 240 |
| 0.130 | 0.01 | 50 | 4.8 | 25 | 200 |
| 0.130 | 0.005 | 50 | 4 | 26 | 200 |

P.38510 -- 4B CFS = 1.13 CUM/SEC MAY 3, 1979

FLOW CHARACTERISTICS FOR U(1) = 1.00 M/SEC

| N | DEPTH(N) M | DIST(N) M | DIA(N) M | DL(N) M | D(N) M | V(M) M/SEC | U(N) M/SEC | FN(N) | E(N) M | SQ(N) CUM/SEC | Q(N) L/SEC | QL(N) L/M.SEC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 79.26 | 890.20 | | | .257 | | 1.00 | 4.28 | .850 | | 38.95 | |
| 2 | 78.11 | 877.04 | .610 | 13.72 | .250 | .13 | 1.26 | 5.35 | .081 | .039 | 46.25 | 2.84 |
| 3 | 76.96 | 863.89 | .610 | 13.72 | .230 | .29 | 1.49 | 6.60 | .113 | .085 | 46.35 | 3.37 |
| 4 | 75.81 | 850.73 | .610 | 13.72 | .220 | .45 | 1.71 | 7.75 | .149 | .132 | 48.66 | 3.38 |
| 5 | 74.66 | 837.57 | .610 | 13.72 | .200 | .62 | 1.93 | 9.17 | .189 | .180 | 45.40 | 3.55 |
| 6 | 73.51 | 824.42 | .610 | 13.72 | .200 | .77 | 2.15 | 10.25 | .236 | .226 | 50.73 | 3.31 |
| 7 | 72.36 | 811.26 | .760 | 13.72 | .190 | .61 | 2.84 | 14.68 | .412 | .424 | 48.39 | 3.71 |
| 8 | 71.28 | 798.10 | .760 | 13.72 | .180 | .72 | 2.49 | 12.50 | .317 | .326 | 47.55 | 3.68 |
| 9 | 70.05 | 784.95 | .760 | 13.72 | .180 | .82 | 2.67 | 13.37 | .362 | .373 | 50.86 | 3.47 |
| 10 | 68.98 | 771.79 | .760 | 13.72 | .170 | .94 | 2.84 | 14.68 | .412 | .424 | 48.39 | 3.71 |
| 11 | 67.75 | 758.64 | .760 | 13.72 | .170 | 1.84 | 3.03 | 15.62 | .467 | .472 | 51.52 | 3.53 |
| 12 | 66.68 | 745.48 | .910 | 13.72 | .160 | .81 | 3.16 | 16.82 | .510 | .524 | 47.66 | 3.75 |
| 13 | 65.45 | 732.32 | .910 | 13.72 | .150 | .88 | 3.38 | 18.12 | .554 | .572 | 43.69 | 3.47 |
| 14 | 64.38 | 719.17 | .910 | 13.72 | .150 | .95 | 3.44 | 18.87 | .682 | .615 | 45.51 | 3.18 |
| 15 | 63.15 | 786.81 | .910 | 13.72 | .150 | 1.02 | 3.57 | 19.64 | .651 | .661 | 47.36 | 3.32 |
| 16 | 61.99 | 692.85 | .910 | 13.72 | .150 | 1.09 | 3.72 | 20.42 | .784 | .788 | 49.24 | 3.45 |
| 17 | 60.84 | 679.70 | .910 | 13.72 | .150 | 1.17 | 3.86 | 21.22 | .768 | .757 | 51.16 | 3.59 |
| 18 | 59.69 | 666.54 | .910 | 13.72 | .150 | 1.24 | 4.01 | 22.03 | .820 | .809 | 53.13 | 3.73 |
| 19 | 58.54 | 653.38 | 1.067 | 13.72 | .140 | .96 | 4.12 | 23.43 | .865 | .862 | 47.54 | 3.87 |
| 20 | 57.39 | 640.23 | 1.067 | 13.72 | .140 | 1.02 | 4.23 | 24.85 | .912 | .989 | 48.81 | 3.46 |
| 21 | 56.24 | 627.07 | 1.067 | 13.72 | .140 | 1.07 | 4.34 | 24.69 | .961 | .958 | 58.18 | 3.56 |
| 22 | 55.09 | 613.91 | 1.067 | 13.72 | .130 | 1.13 | 4.45 | 26.29 | 1.011 | 1.008 | 44.32 | 3.65 |
| 23 | 53.94 | 600.76 | 1.067 | 13.72 | .130 | 1.18 | 4.57 | 26.96 | 1.064 | 1.053 | 45.46 | 3.23 |
| 24 | 52.79 | 587.60 | 1.067 | 13.72 | .130 | 1.23 | 4.68 | 27.65 | 1.119 | 1.098 | 46.61 | 3.31 |
| 25 | 51.63 | 574.44 | 1.067 | 13.72 | .130 | 1.28 | 4.80 | 28.34 | 1.176 | 1.145 | 47.78 | 3.40 |

Outfall Pipeline

Total Discharge = 1.192 CUM/SEC
Diameter of Outfall Pipeline = 1.067 M
Velocity in Outfall Pipeline = 1.33 M/SEC
Total Length of Manifold = 329.28 M
Total Length of Outfall Pipeline = 629.53 M
Total Head at Shore = 3.86 M

# MONITORING NON-EXISTENT CHEMICALS

Dr. Bruce McKague
B.C. Research
3650 Wesbrook Cres.
Vancouver, B.C.
V6S 2L2

In May, 1981, we received an invitation to submit a proposal to analyze chlorinated organics in receiving waters, sediment and biota. An up-to-date inventory of compounds was provided which included many recent reports from the scientific literature.

Overheads 1 & 2

A number of the compounds listed were well recognized as present in pulp mill effluent. Others were rather novel and have only recently been identified. My presentation today, arising from my own interest in chlorinated organics, concerns the trend of techniques used to identify many of these newly reported chlorinated organics.

There is no doubt that trace environmental analyses have benefited enormously from the technique of gas chromatography/mass spectrometry. The technique allows the scientist to obtain a mass spectrum of a component as it elutes from a gas chromatograph. Many identifications can be made by comparing mass spectra generated in the manner with libraries containing reference spectra. But what about new compounds? Can they be identified in this manner? Let us examine some recent literature reports.

Overhead 3

The above list of chlorinated organics appeared in the literature in 1978. Including isomers, but excluding the two bottom structures, this report contained 22 new compounds, the structures of many of which are a little surprising. It is important to note the use of mass spectrometry and also the fact that these are suggested structures.

OVERHEAD 1

May 19, 1981

B.C. Research
3650 Wesbrook Crescent
Vancouver, B.C.
V6S 2L2

Attention:

Dear

The Council of Forest Industries Technical Advisory Committee has identified a need for further information regarding the potential persistence of chlorinated organic compounds that may be discharged from a typcial British Columbia bleached kraft pulp mill into receiving waters. Previous work has provided an extensive "inventory" of chlorinated organic compounds that are, or may be, present in the effluent from bleached kraft pulp mills. The Technical Advisory Committee is soliciting contractual proposals for investigations into the fate and possible persistence of these chlorinated organic compounds in the receiving waters. The treated effluent from one B.C. interior bleached kraft pulp mill and the untreated effluent from two B.C. coastal bleached kraft pulp mills will be studied. The three sites are not finalized, and so detailed sampling requirements cannot be described at this time.

Contractual participation in this study is invited in the following areas:

a) Sampling: A comprehensive sample collection regime is mandatory. Samples must be taken at mill fresh water intakes as control point references. Also, samples of mill effluent prior to contact with receiving waters will be obtained. Further, to evaluate the fate and possible persistence of pulp mill originated chlorinated organic compounds, samples will be obtained of sediments, resident and transient biota, as well as of receiving waters several kilometers "downstream" of a mill outfall.

   It will be necessary that the consultant awarded the sample collection aspects of this study work closely with the consultant involved with the analytical evaluation of the study. This necessarily close liaison will include agreement on sample sizes, sample preparation, preservation and identification, as well as delivery arrangements to the analytical group.

APPENDIX A OVERHEAD 2

## COMPOUNDS OF CONCERN

The inventory and analyses should include the following compounds:

- Fatty acids and chlorinated fatty acids, specifically 9, 10-dichlorostearic acid, epoxystearic acid, oleic acid, linoleic acid and linolenic acid; (RA & FA)*
- Chlorinated cymenes, specifically chloro-p-cymene, dichlorocymene and trichlorocymene; (N)*
- Camphor, 2 - terpineol and fenchone; (N)
- Chlorinated calamenenes; (N)
- Chlorinated and unchlorinated resin acids, specifically abietic acid, dehydroabietic acid, 1,2 - and 1,4 - dichlorodehydroabietic acid; (RA)
- Guaiacols, catechols (P)* and veratroles with 2 or more chlorine substituents; (N)
- Phthalate acid esters, notably di-n-octyl phthalate; (N)
- Chlorinated forms of cyclopentenedione, pyrone, benzene, and toluene; (N)
- Chlorinated forms of butadiene, butatriene and propene. (N)

---

*RA - resin acids; FA - fatty acids; P - phenols; N - neutrals.

OVERHEAD 3

IDENTIFICATION OF SOME NEUTRAL CHLORINATED ORGANIC COMPOUNDS IN SPENT BLEACH LIQUORS

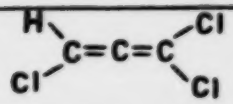
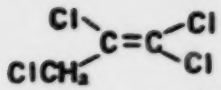
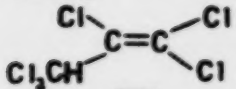
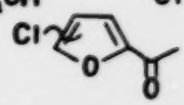
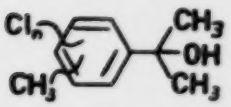
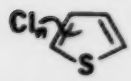
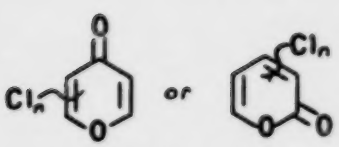
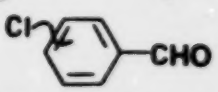
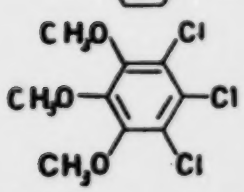
| Suggested Structures | Number of Isomers Found | Compound |
|---|---|---|
|  | | Trichloroallene |
|  | | Tetrachloropropene |
|  | | Pentachloropropene |
|  | | Monochloroacetylfuran |
|  | 5 | Monochloro-8-hydroxycymene, n=1<br>Dichloro-8-hydroxycymene, n=2 |
|  | | Trichlorothiophene, n=3<br>Tetrachlorothiophene, n=4 |
| | 2<br>2 | Dichloroformylthiophene, n=2, R=CHO<br>Trichloroformylthiophene, n=3, R=CHO<br>Dichloroacetylthiophene, n=2, R=$COCH_3$<br>Trichloroacetylthiophene, n=3, R=$COCH_3$<br>Dichloropropionylthiophene, n=2, R=$COCH_2CH_3$ |
|  | | Monochloropyrone, n=1<br>Dichloropyrone, n=2<br>Trichloropyrone, n=3 |
|  | 2 | Monochlorobenzaldehyde |
|  | | Trimethoxytrichlorobenzene |

Table 1. Neutral chloroorganic compounds found in the ether extract of a chlorination stage spent liquor obtained from sulphate pulp.

Identification of some of the compounds listed in Table 1 has been carried out entirely by means of their mass spectra. Hence, some of the structures might be isomeric. Some spectra have been identified by comparing with reference spectra(3) and others by comparison of their mass spectra with those of the corresponding synthesized products.

Overhead 4

Another list of 36 compounds which appeared in the literature in 1981 and all of which were identified by mass spectrometry. Of the 36, ten or a little less than 1/3 were tentative identifications based on mass spectral interpretation (in other words, no reference spectra or standards were available for comparison).

How easy is it to identify chlorinated compounds by their mass spectra? Unless the compound is a chlorinated aromatic, it can be very tricky. We submitted samples of simple compounds for identification by GCMS using a reference library. When a sample containing 1,1,3-trichloroacetone was submitted, it was identified as 1,3-dichloroacetone because the spectra were similar, and only the spectrum of the dichlorocompound was in the library.

Overheads 5 & 6

Some might say it dosen't matter too much in this case, since it dosen't matter much if it's dichloro-or trichloroacetone in the effluent - we can just group all the chloroacetones together. It's possible to make more serious errors, however, as shown by the following spectra we obtained for 1,1,3,3-tetrachloroacetone, the EPA published spectrum for the same compound, and the spectrum of an unknown.

Overheads 7, 8 & 9

Even chlorinated aromatics can be tricky if you have a preconceived notion about the identity of a compound. We had already identified trichloro- and tetrachlorocatechol in chlorination-stage effluent when we obtained the spectrum of another chlorophenol which looked similar to dichlorocatechol. Although, logically, dichlorocatechol was present, the new compound turned out to be 2,6-dichlorohydroquinone.

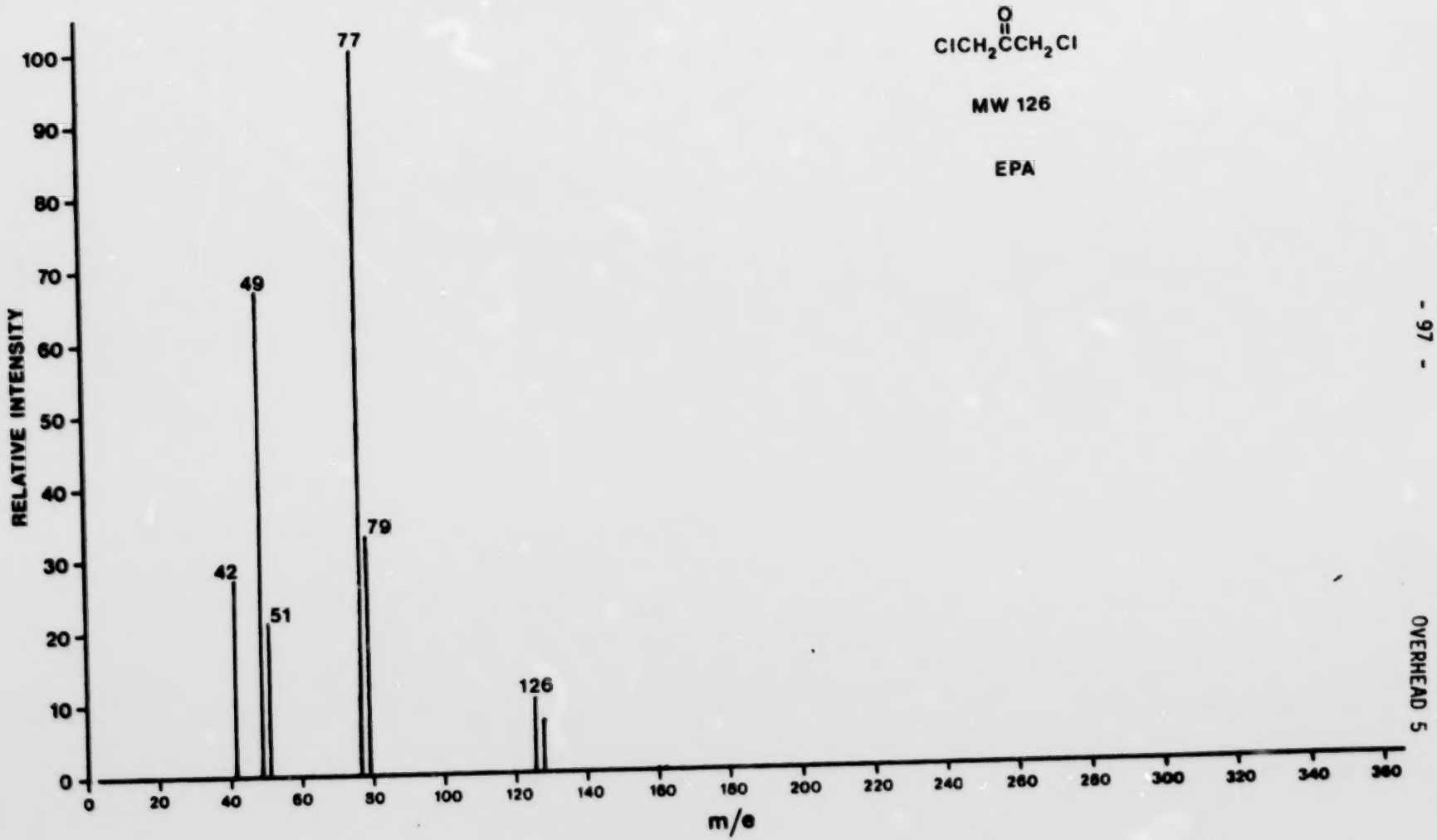
OVERHEAD 4

# Identification and Mutagenic Properties of Some Chlorinated Aliphatic Compounds in the Spent Liquor from Kraft Pulp Chlorination

**Table II. Identified Compounds and Their Mutagenic Activity According to the Ames Test**

| Identified compds | Technique of identification [a] | mutagenic activity [b] | ref to the Ames test |
|---|---|---|---|
| dichloromethane | A | TA 100, pos | *22* |
| chloroform | A | neg (carcinogen) | *23* |
| carbon tetrachloride | A | neg (carcinogen) | *24* |
| bromodichloromethane | B | TA 100, pos | *22* |
| dibromochloromethane | B | TA 100, pos | *22* |
| trichloroethylene | A | TA 100, pos | *22* |
| | A | TA 1535, pos | *25* (see Table IV) |
| tetrachloroethylene | A | TA 100, pos | *25* |
| | A | TA 1535, neg | see Table IV |
| pentachloropropene | C | TA 100, TA 1535, pos | *26* |
| five isomers of monochlorinated methylbutenes | C | unknown | |
| monobrominated methylbutene | C | unknown | |
| tetrachloroallene | C | unknown | |
| methyl dichloroacetate | B | unknown | |
| ethyl chloroacetate | A | TA 1535, neg | see Table IV |
| ethyl dichloroacetate | B | unknown | |
| ethyl trichloroacetate | A | TA 1535, neg | see Table IV |
| monochloroacetone | A | TA 100, neg | *27* |
| | A | TA 1535, neg | see Table IV |
| 1,1-dichloroacetone | B | unknown | |
| 1,3-dichloroacetone | A | TA 100, pos | *27* |
| | A | TA 1535, pos | see Table IV |
| 1,1,1-trichloroacetone | B | unknown | |
| 1,1,3-trichloroacetone | B | unknown | |
| 1,1,1,3-tetrachloroacetone | B | unknown | |
| 1,1,3,3-tetrachloroacetone | A | TA 100, pos | *27* |
| | A | TA 1535, neg | see Table IV |
| pentachloroacetone | A | TA 1535, neg | see Table IV |
| hexachloroacetone | A | TA 100, pos | *27* |
| | A | TA 1535, pos | see Table IV |
| trichlorocyclobutenone | C | unknown | |
| four chlorinated cyclopentene-1,2-diones | C | unknown | |
| monochloroacetaldehyde | A | TA 100, TA 1535, pos | *28-31* (see Table IV) |
| trichloroacetaldehyde | A | TA 1535, neg | see Table IV |
| 2-chloropropenal | A | TA 100, pos | *32* |
| | A | TA 1535, pos | see Table IV |

[a] (A) Complete identification based on mass-spectral interpretation and confirmed by comparison with a reference spectrum of the substance. (B) Complete identification based on mass-spectral interpretation and confirmed by comparison with a reference spectrum from "Eight Peak Index" (*33*). (C) Tentative structure; identification based on mass-spectral interpretation. Mass spectra (six most abundant mass fragments) of these substances are given in Table III. [b] Ames test, *Salmonella typhimurium*.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EPA
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80
70
60
50
40
30
20
10
0
77
49
79
42
51
126
0
20
40
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140
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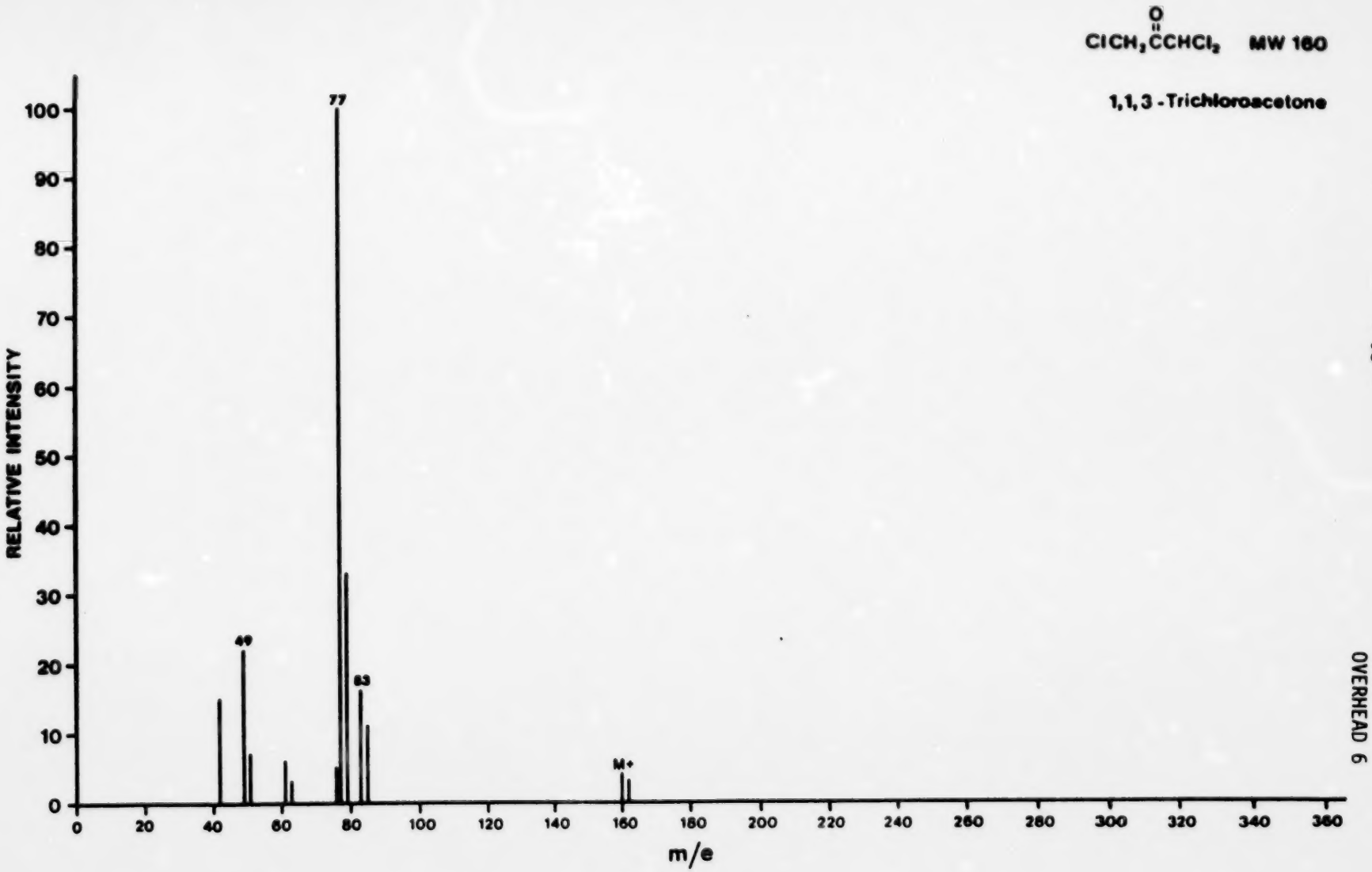
180
200
220
240
260
280
300
320
340
360
m/e



OVERHEAD 5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1,1,3 - Trichloroacetone
RELATIVE INTENSITY
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83
M+
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10
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30
40
50
60
70
80
90
100
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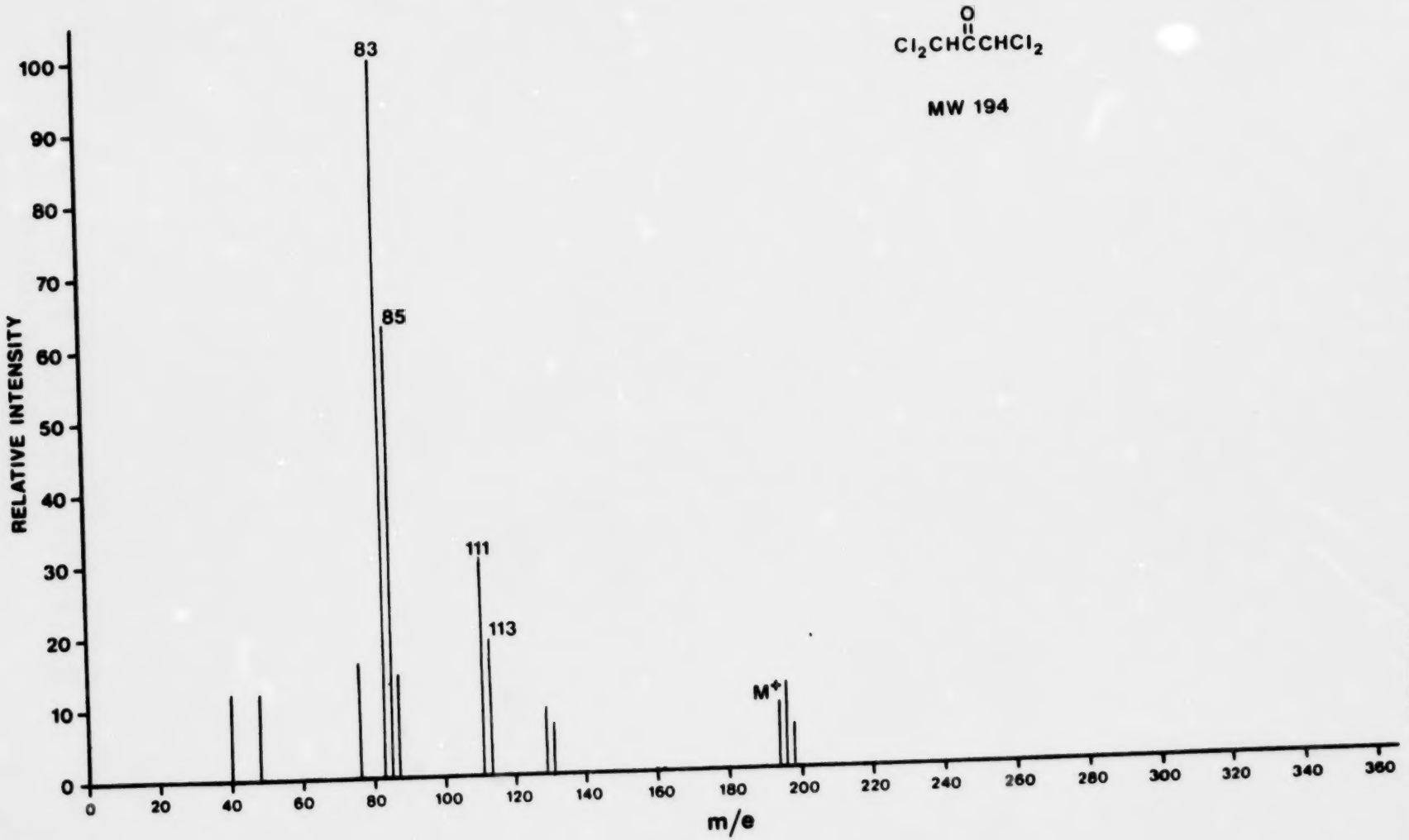
OVERHEAD 6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113
M+
RELATIVE INTENSITY
m/e
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50
60
70
80
90
100
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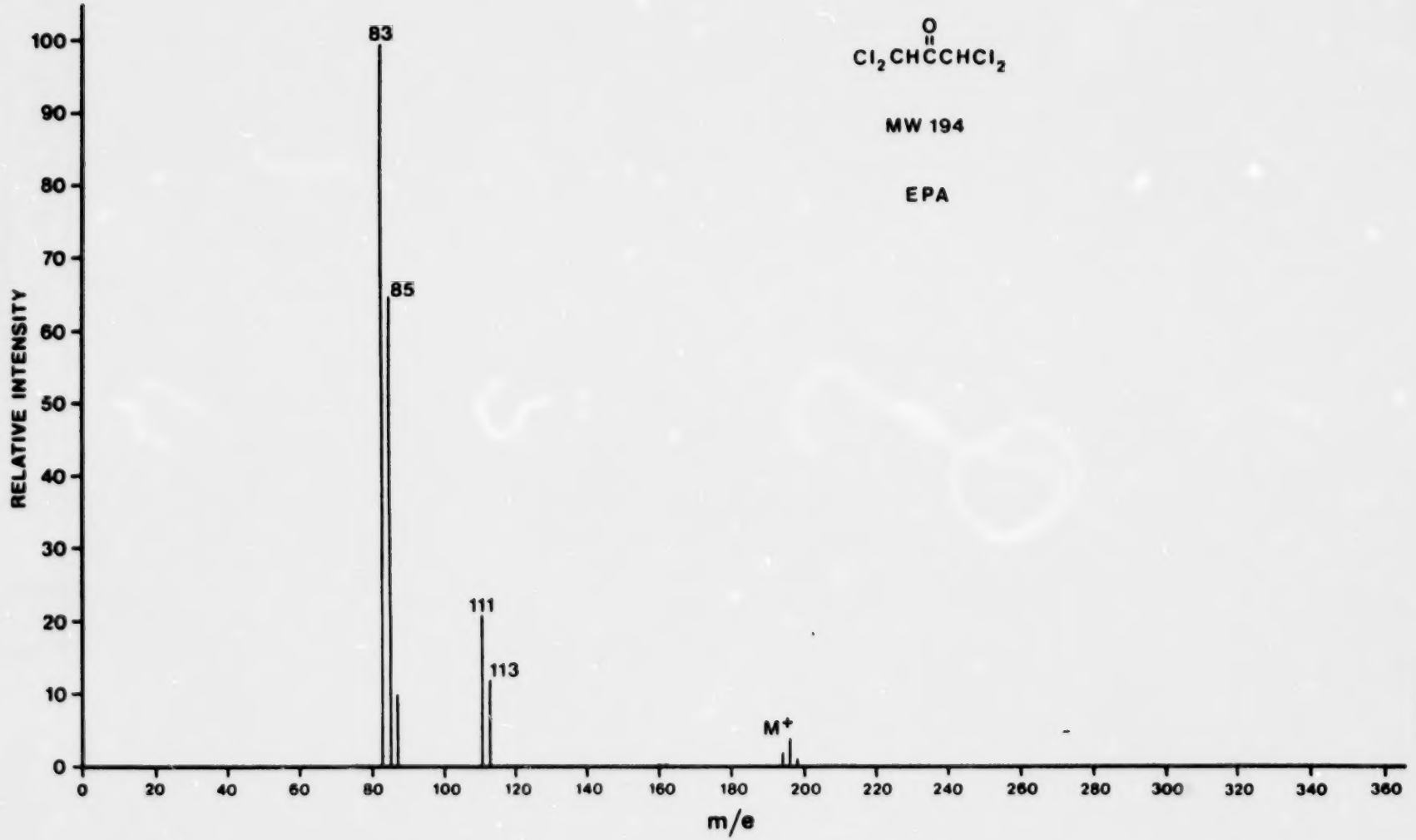
300
320
340
360



OVERHEAD 7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MW 194
EPA
RELATIVE INTENSITY
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83
85
111
113
M+
0
20
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200
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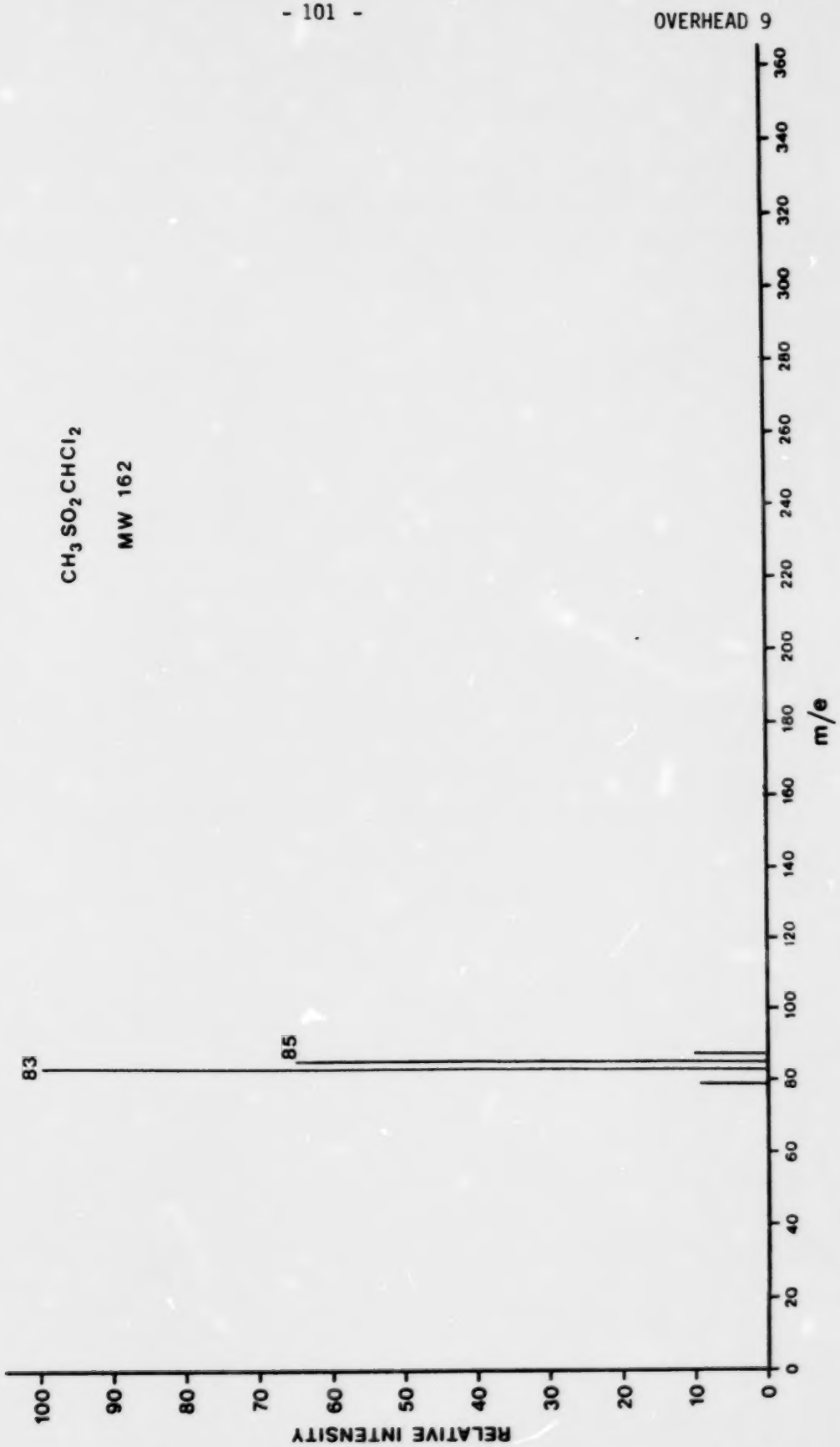
280
300
320
340
360
m/e



OVERHEAD 8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100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

Overheads 10 & 11

What happens when new compounds are reported in the literature? Consider the following process whereby an inventory of chlorinated compounds is prepared for environmental purposes.

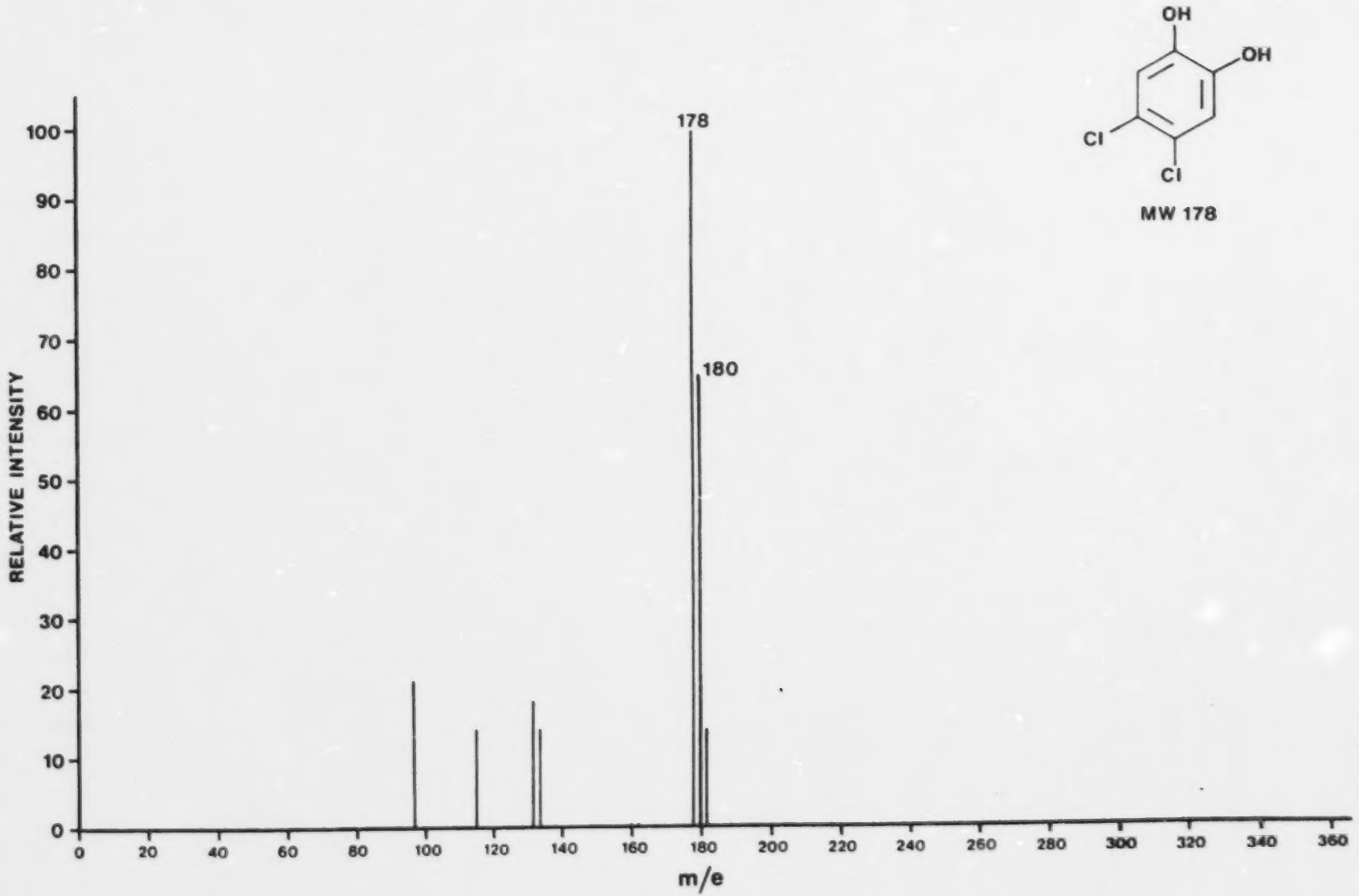
Overhead 12

An example of such an inventory by NCASI is shown next.

Overheads 13 & 14

The final result then brings back to where I started with the invitation to monitor the presence of chlorinated organics listed in the inventory.

In summary, I would like to say that my intentions have been to illustrate a sequence of events which may and can occur, initiated by tentative identifications of chemicals. I ask the question, how many of the compounds of environmental concern reported during the last 5 years have been firmly identified? How many chemicals tentatively identified by interpretation of mass spectra have been confirmed? Let us attempt to clarify, through research, firm identities of newly reported chemicals lest we find ourselves attempting to monitor non-existent chemicals.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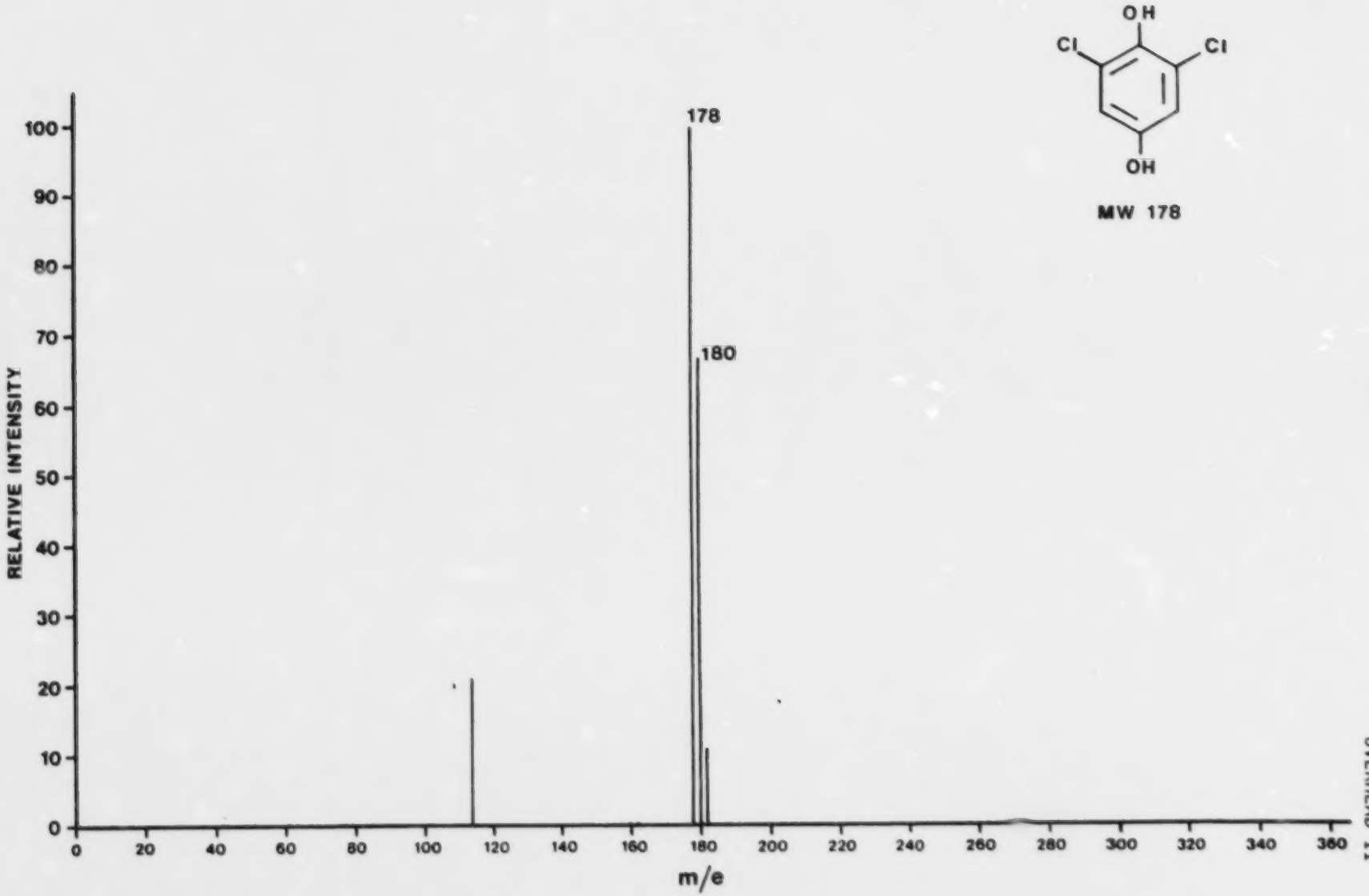
m/e



OVERHEAD 10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20
40
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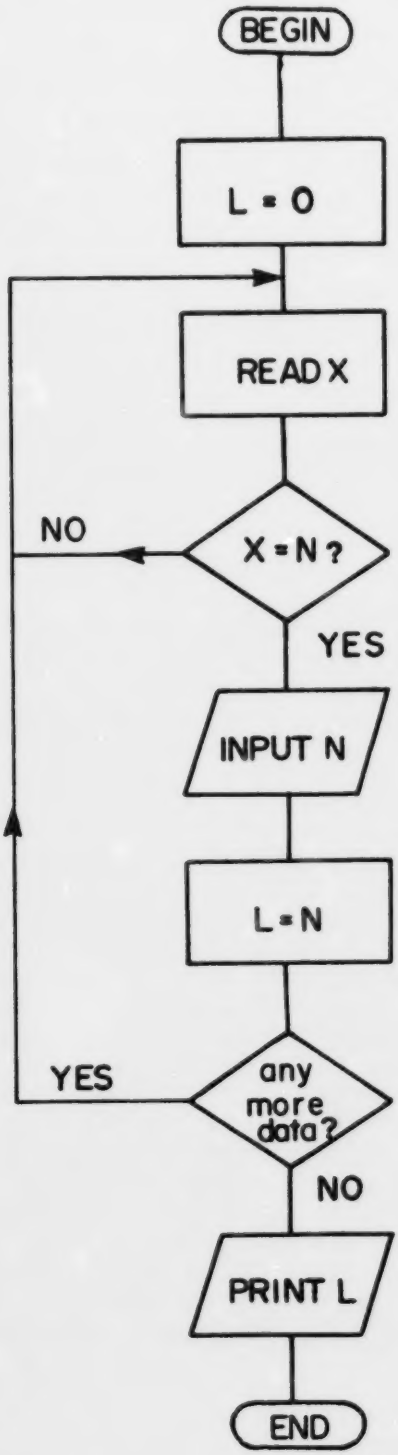
m/e



OVERHEAD 11

OVERHEAD 12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READ X
X = N ?
NO
YES
INPUT N
L = N
any more data?
YES
NO
PRINT L
END

OVERHEAD 13

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
Technical Director
(212) 532-9001

STREAM IMPROVEMENT
TECHNICAL BULLETIN NO. 332

May 29, 1980

# CHLORINATED ORGANICS IN BLEACH PLANT EFFLUENTS OF PULP AND PAPER MILLS

In late October 1979, the National Cancer Institute, Nuclear Regulatory Commission, Oak Ridge National Laboratory, Tennessee Valley Authority, U. S. Department of Energy and the U. S. Environmental Protection Agency sponsored the Third Conference on Water Chlorination - Environmental Impact and Health Effects.

Earlier conferences on this subject dealt almost entirely with the scientific questions arising around the disinfection of public water supplies, municipal effluents, and related subjects. The conference organizers expanded the subject scope of the 1979 conference and included several papers on industrial uses of chlorine. Among these were four papers on bleachery effluents, their characterization and biological effects.

The attached technical bulletin is the paper presented at the above conference by NCASI staff members, Dr. Robert R. Claeys and Larry E. LaFleur, Research Chemists at the West Coast Regional Center and Dr. Dennis L. Borton, Southern Experimental Streams Project Manager. The paper summarizes (a) the chemical characteristics of untreated bleachery effluents and (b) some of the biological effects on the aquatic environment caused by effluents which have not received biological treatment. The contents of the paper go further to explain the significant change in the chemical composition of bleached mill effluents after biological treatment. The favorable observations made in the Council's controlled stream program, where fish are exposed to biologically treated bleached kraft effluents, are also summarized. Three other papers were presented which dealt with bleachery effluents and which will be included in the conference proceedings to be distributed later this year. Described were Swedish and Canadian studies on the mutagenicity of principally untreated bleachery mill effluents. The material from which the latter

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TABLE 3. NEUTRAL HALOGENATED ORGANICS IDENTIFIED IN PROCESS EFFLUENT (PE) OR BIOLOGICALLY TREATED EFFLUENT (BTE)

| COMPOUND | Reference PE | BTE |
|---|---|---|
| Di- and Trichlorotoluene | | 20,21 |
| Di- and Trichloroxylene | 20,21 | 20,21 |
| Hexachlorobenzene | 24 | |
| Pentachloroanisole | | 20,21 |
| Dichloroveratrole | | 20,21 |
| Trichloroveratrole | | 20,21 |
| Mono-,Di- and Trichloro-p-cymene | 9,10,24,25 | |
| Mono- and Dichloromethyl Isopropenyl Benzene | 25 | |
| Bromo-p-cymene | 9,10,24,25 | |
| Bromochloro-p-cymene | 9,10 | |
| Chloro- and Bromocymene-α-ol | 8,9,10 | |
| Chloro- and Bromocalamenene | 9,10,24 | |
| Chloro-3-hydroxycymene | 8 | |
| Dichloro-8-hydroxycymene | 8 | |
| Tri- and Tetrachlorothiophene | 8 | |
| Di- and Trichloroacetylthiophene | 8 | |
| Dichloropropionylthiophene | 8 | |
| Mono-,Di- and Trichloropyrone | 8 | |
| Trimethyoxytrichlorobenzene | 8 | |
| Dichlorodimethylpropyldihydro-napththalene | 24 | |
| Mono- and Dichloromethylpropyl Naphtalene | 24 | |
| Tetrachloroacetone | | 20,21 |
| Methyl Mono- and Dichlorodehydroabietate | 20,21 | |

The NCASI is currently in the process of analyzing fish exposed to biologically treated effluent from a bleach kraft mill. The objective of this analysis is to determine the extent of bioaccumulation of chlorinated compounds found in the treated effluents in fish taken from these streams.

## V BIOLOGICAL EFFECTS OF BLEACHED PULP MILL EFFLUENTS ON THE ENVIRONMENT

The NCASI is in the tenth year of studying the biological effects of pulp mill effluent on the aquatic community, using manmade streams that receive controlled amounts of biologically treated effluents on a continuous basis.

# CHLORINATED ORGANIC SPECIES DETECTED IN KRAFT MILL WASTEWATER

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Softwood is complex biological material composed of cellulose (40-45%) hemicellulose (20-30%) and lesser amounts of extractives (Wise and Jahn 1952). In the process of chemical pulping of wood to yield mainly cellulose, the other three fractions are largely removed and extensively altered chemically. Hemicellulose is hydrolysed to free sugars and wood extractives are partially recovered as turpentine or tall oil. Lignin is greatly changed chemically following the reactions in the digester and is released from the wood as thiolignin. However residual lignin remains attached to the brownstock and is removed or destroyed as chlorolignin and various small molecules which are released from the lignin side chains by oxidative cleavage in the presence of chlorine. This review describes the progress over the last decade in our understanding of the nature of the chlorinated organic compounds formed during the bleaching of kraft pulp. Some of these compounds have lethal effects on aquatic life and some have been identifed as chemical mutagens. However these aspects of the subject will be covered by some of the other speakers at this workshop.

Chlorinated organics formed in the kraft process are of three classes. These classes are defined as the volatiles, the extractables, and the high-molecular-weight fractions of bleachery wastes.

## Volatile Chlorinated Organics

The volatile compounds are generally measured by purge and trap analysis and include the haloforms such as chloroform and some miscellaneous chlorinated compounds such as trichloroethylene. The compounds that fit into this class are listed in Table 1 which is somewhat

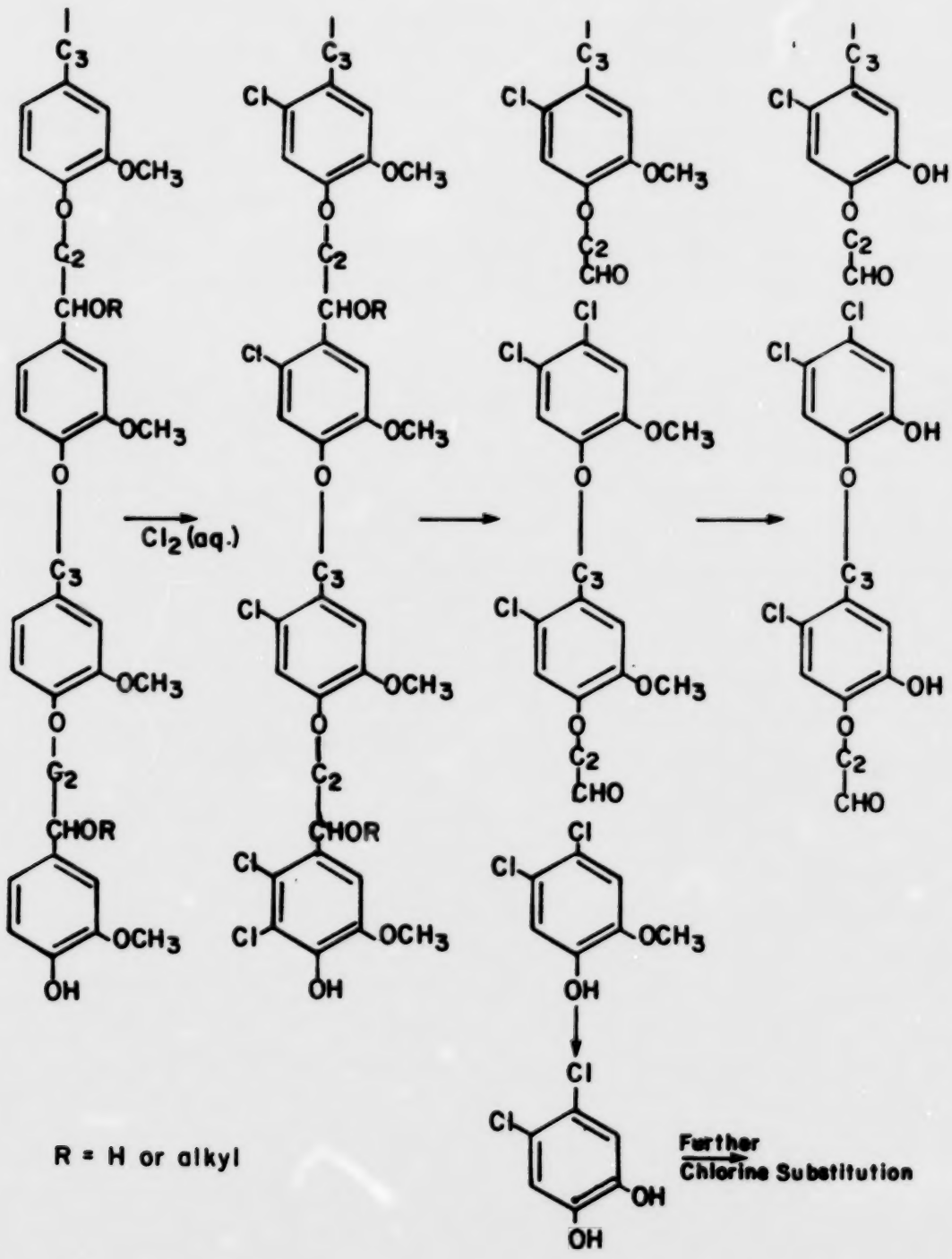
arbitrary. Since little has been published to date on the types of compounds present and their yields in the kraft process, I have listed those substances from Swedish research results that have boiling points low enough to indicate that they could probably be analysed by the purge and trap technique. There might be some problems, however, in trying to do this as some compounds may be too highly soluble in water. The work on the identification and quantitation of these substances has been largely conducted by the Swedish Forest Products Laboratory and the National Council for Air and Stream Improvement in Corvallis, Oregon. Chloroform is by far the major constituent of this type and it is noteworthy that the presence of this substance in spent bleaching liquor was recognized many years ago (Harris et al. 1934).

TABLE 1 VOLATILE CHLORINATED ORGANICS FORMED DURING KRAFT PULP BLEACHING OPERATIONS

| | |
|---|---|
| dichloromethane | monochloromethylbutenes (5 isomers) |
| chloroform | monobromomethylbutene |
| carbon tetrachloride | tetrachloroallene |
| trichloroethylene | monochloroacetone |
| tetrachloroethylene | monochloroacetaldehyde |
| bromodichloromethane | 2-chloropropenal |
| dibromochloromethane | trichloroacetaldehyde |

The list of compounds in Table 1 is taken from the work of Kringstad et al. 1981. The brominated compounds arise either as a consequence of the presence of bromide ions in the pulp bleaching or washing sequences or because of the presence of bromine as an impurity in the chlorine used in the first stage. Chloroform yields in kg per metric ton of pulp have been estimated by Lindstrom et al. 1981 as 0.01, 0.03 and 0.15 for the chlorination, extraction and hypochlorite stages respectively.

FIGURE 1 PROPOSED MECHANISM FOR THE ACIDIC CHLORINATION OF SOFTWOOD LIGNIN ACCORDING TO DENCE AND SARKANEN, 1960

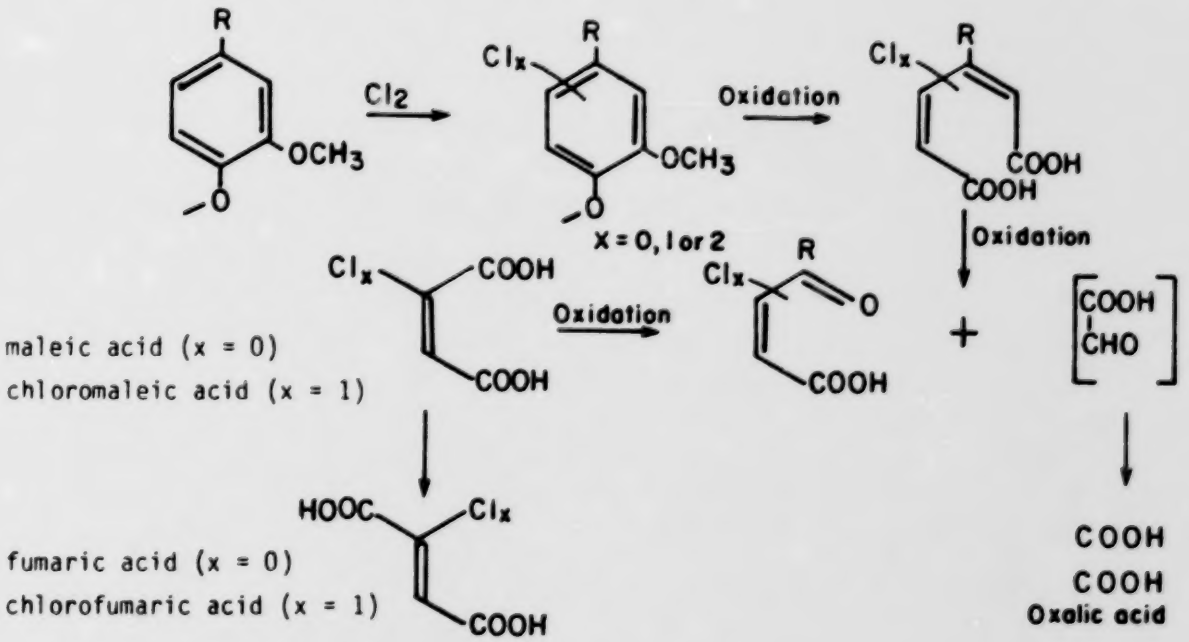


Extractable Chlorinated Compounds

The structure of lignin has been the subject of much research and debate over the past one hundred and twenty-five years. Many great chemists have contributed to our present understanding of this three dimensional polymer. In 1960 Dence and Sarkanen proposed the mechanism illustrated in Figure 1 to show the degradation of softwood lignin under acidic chlorination conditions. The end products they proposed included a dichlorocatechol (extractable) capable of being further chlorinated and a mixture of higher-molecular-weight fragments (chlorolignin).

In 1973 Ota, Durst and Dence isolated and identified chloromaleic and chlorofumaric acids from spent chlorination liquor by thin layer chromatography. The postulated formation of these compounds is by the oxidation of chlorinated phenolic residues as in Figure 2.

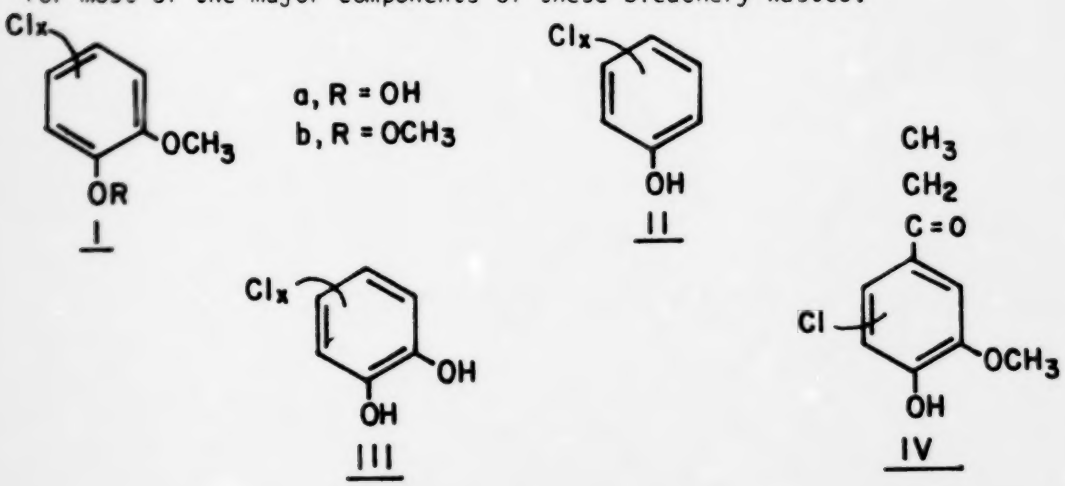
FIGURE 2 LOW MOLECULAR WEIGHT COMPOUNDS IN SPENT CHLORINATION LIQUOR ACCORDING TO OTA, DURST AND DENCE, 1973




Proposed sequence for oxidative breakdown of softwood lignin to acidic fragments in chlorination.

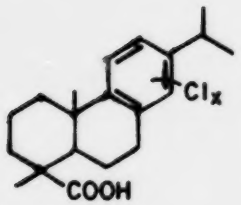
Although these compounds are of the correct molecular weight range to be considered as extractables, they are highly polar and have not been reported by later workers, presumably because they are not removed in the extracting solvents commonly used in recent studies.

The advent of combination gas chromatography-mass spectrometry (GC-MS) has allowed great progress to be made in the analysis and identification of trace organic compounds in complex mixtures such as wastewaters. In the early 1970's this technique began to be applied to kraft bleaching wastes. A trichloroveratrole was identified in a methylated extract of bleached kraft whole mill effluent (Rogers 1973). Although it was not possible to identify the precursor as a chloroguaiacol or a chlorocatechol, this was apparently the first direct supporting evidence for the mechanism of lignin chlorination put forward by Dence and Sarkanen (Figure 1). Evidence as to the identity of the precursors of the trichloroveratrole was obtained later by substituting diazoethane for diazomethane in the derivatization procedure. Rogers and Keith 1974, identified 4,5,6-trichloroguaiacol (Ia, x = 3) and tetrachloroguaiacol (Ia, x = 4) in caustic extraction effluent from two mills. Leach and Thakore 1975, also identified tetrachloroguaiacol and 3,4,5-trichloroguaiacol. A larger study was initiated at the Swedish Forest Products Laboratory. Lindstrom and Nordin 1976, analysed chlorination effluent as well as caustic extraction effluent. They found di- and 2,4,6-trichlorophenol (II) present in both types of wastewater. Besides the chlorinated guaiacols already mentioned, they found three isomers of dichloroguaiacol, di-, tri- and tetrachlorocatechol (III x = 2, 3 or 4) and monochloropropiovanillone (IV). They were able to provide yields per ton of pulp for most of the major components of these bleachery wastes.



The correct assignment of positions of chlorine atoms in di- and trichloroguaiacols caused some problems before model compounds became available from chemical synthesis, backed up by nuclear magnetic resonance spectroscopy. Lindstrom and Osterberg 1980, used x-ray crystallography to show conclusively that the major trichloroguaiacol present in caustic extraction wastes is the 3,4,5 isomer. 4,5,6-trichloroguaiacol and tetrachloroguaiacol have been synthesized by the direct chlorination of guaiacol in acetic acid solution (Fort et al. 1955). Using the approach of limited methylation of chlorinated catechols, followed by chromatographic separation of the products, some very systematic work in Finland has led to the availability of all possible isomers of chlorinated guaiacols (Knuutinen and Tarhanen 1981). The chlorinated catechols were in turn prepared via the Dakin synthesis from the corresponding chlorinated 2-hydroxybenzaldehydes. By thoroughly establishing the thin layer chromatographic, gas chromatographic, mass spectrometric and nuclear magnetic resonance data for all the possible model compounds, the Finns have supplied the previously missing basic chemistry on which current analytical determinations of the composition of bleachery wastewaters are now based. Examples of the application of current state-of-the-art analytical methods are to be found in papers by Holmbom 1980; Voss et al. 1981 and Knuutinen 1982.

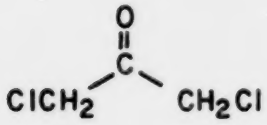
Besides the lignin-derived chlorinated phenolic compounds, a wide variety of structures has now been identified in bleachery wastes. Mono- and dichlorodehydroabietic acids (V, x = 1 or 2) were first identified by Leach and Thakore 1975. These remain the only chlorinated resin acids that have been reported. Kutney et al. 1982 have examined the activity of a fungus Mortierella isabellina in chemicallly degrading and detoxifying one of these compounds 14-chlorodehydroabietic acid. By the simple introduction of one or more oxygen substituents on the ring, the fungus removes the acutely toxic properties of the chlorinated resin acid to sockeye salmon and Daphnia.



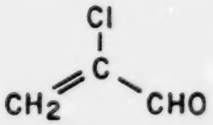

x = 1 or 2

V

There has been much interest in mutagenic compounds in bleachery wastes in recent years. Two such compounds are 1,3-dichloroacetone (VI) and 2-chloropropenal (VII) identified by Kringstad et al. 1981. Chloroacetones have also been implicated in mutagenic properties of

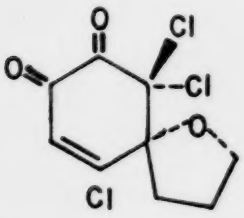



VI

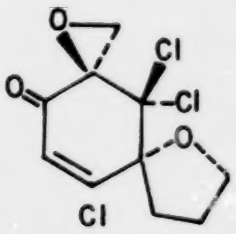



VII

bleachery wastes by McKague, Lee et al. 1981. Another interesting compound, suspected of having mutagenic properties, is 1-oxa-6, 10, 10-trichlorospiro [4,5] dec-6-ene-8, 9-dione (VIII). The reaction product of this compound with diazomethane yielded a crystalline derivative (IX) whose structure was clearly established by x-ray crystallography (McKague, Rettig et al. 1981).

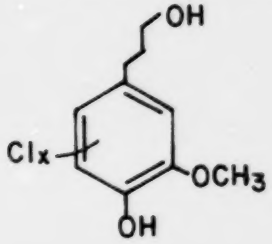



VIII

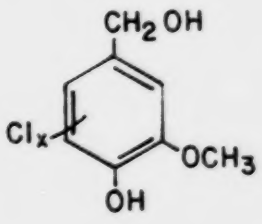



IX

Other chlorinated extractable compounds identified in recent years include chlorinated dihydroconiferyl alcohol X (x = 2 or 3) and chlorinated vanillyl alcohol XI (x = 1, 2 or 3) identified in caustic

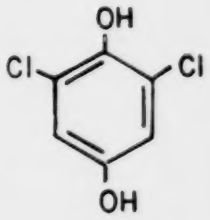



X

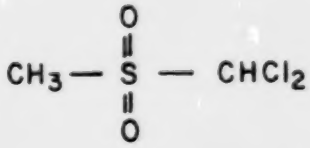



XI

extraction effluent from the pulping of Western red cedar (Mortimer and Wong 1979). 2,6-Dichlorohydroquinone (XII) and dichloromethyl methyl sulphone (XIII) have been identified in chlorination effluent by McKague 1981.




XII



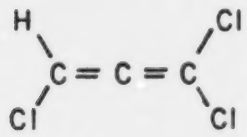

XIII

A large variety of neutral chlorinated organic extractables has been identified at the Swedish Forest Products Laboratory and scanned for mutagenic activity via the Ames test (Kringstad et al. 1981).

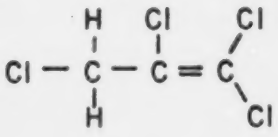
TABLE 2 VARIOUS CHLORINATED NEUTRAL SUBSTANCES IDENTIFIED IN BLEACHERY WASTES

| | |
|---|---|
| pentachloropropene | 1,1,1,3-tetrachloroacetone |
| methyl dichloroacetate | 1,1,3,3-tetrachloroacetone |
| ethyl chloroacetate | pentachloroacetone |
| ethyl dichhloroacetate | hexachloroacetone |
| ethyl trichloroacetate | trichlorocyclobutenone |
| 1,1-dichloroacetone | chlorinated cyclopentene-1,2-diones (4 isomers) |
| 1,1,-trichloroacetone | |
| 1,1,3-trichloroacetone | |

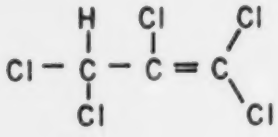
Another list of identified chlorinated neutral compounds has been published by Lindstrom and Nordin 1978. This includes trichloroallene (XIV), tetrachloropropene (XV), pentachloropropene (XVI), monochloroacetylfuran (XVII), monochloro-8-hydroxycymene (XVIII, x = 1),



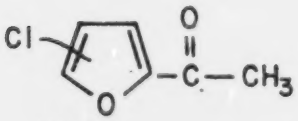
XIV



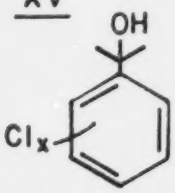
XV



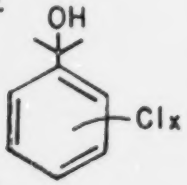
XVI



XVII

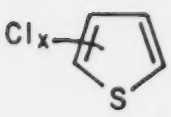


or

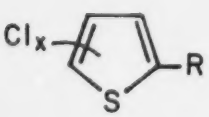


XVIII

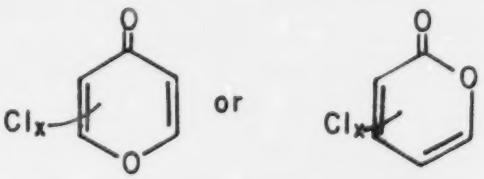
dichloro-8-hydroxycymene (XVIII, x = 2), trichlorothiophene (XIX, x = 3), tetrachlorothiophene (XIX, x = 4), dichloroformylthiophene (XX, x = 2, R = CHO), trichoroformylthiophene (XX, x = 3, R = CHO), dichloroacetylthiophene (XX, x = 2, R = $COCH_3$), trichloroacetylthiophene (XX, X = 3, R = $OCH_3$), dichloropropionylthiophene (XX, n = 2, R = $COCH_2CH_3$), monochloropyrone (XXI, x = 1), dichloropyrone (XXI, x = 2), trichloropyrone (XXI, x = 3), monochlorobenzaldehyde (XXII) and trimethoxytrichlorobenzene (XXIII). Full details on the isolation,



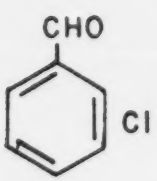
XIX



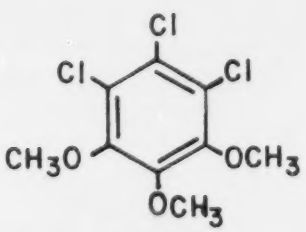
XX



XXI



XXII

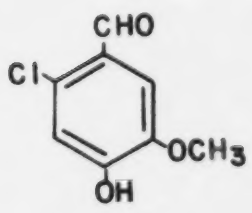


XXIII

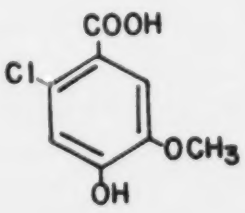
spectral and chromatographic properties of compounds XIV to XXIII do not appear to have been published in the scientific journals and the published structures should therefore be considered as a subject to confirmation.

High Molecular Weight Chlorolignin

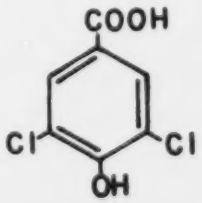
An interesting study was reported by Shimada 1976 on the alkaline cupric oxide oxidation of red pine chlorinated oxylignin. The lignin preparation was isolated from caustic extraction liquor prepared in a normal five-stage laboratory bleach sequence from red pine (Pinus densiflora) pulp. A precipitate was formed upon acidification to pH2 with $H_2SO_4$. This was recovered by centrifugation, purified by dialysis and further purified by dissolution in methyl cellosolve. Oxylignin was washed with petroleum ether and diethyl ether and dried in a vacuum over phosphorous pentoxide. The material analysed for: C: 50.02%, H: 5.20%, O: 29.97%, $OCH_3$: 7.24%, Cl: 10,60%, S: 0.47%, Klason lignin: 63.0% and ash: 1.20%. After alkaline cupric oxide oxidation the following chlorinated organic compounds were identifed by gas cromatography (GC-FID and GC-EC) and by GC-MS. They included 2,4,6-trichlorophenol, 4,6-dichloroguaiacol, 3,4-dichloroguaiacol, 4,5-dichloroguaiacol, 3,5,6 or 3,4,6-trichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachloroguaiacol, 5-chlorovanillin, 6-chlorovanillin (XXIV), 6-chlorovanillic acid (XXV), 5,6-dichlorovanillic acid and 3,5-dichloro-4-hydroxybenzoic acid (XXVI). A number of closely related non-chlorinated compounds were also detected. Therefore the evidence indicated that chlorinated oxylignin is a polymeric substance consisting of units of chlorinated phenolic structure.




XXIV




XXV




XXVI

A method for determination of total organically-bound chlorine has been described by Sjostrom et al. 1982. This involves ultra-filtration, sorption on a crosslines polymer to permit separation of inorganic from organic chlorine, and Schoniger combustion of the organic residue, followed by potentiometric titration with silver nitrate. About 5 kg/metric ton of pulp, or 70% of the overall total organic chlorine from a bleaching sequence is found in the spent bleach liquor from the first two stages. The chlorination stage and the caustic extraction stage wastewaters contain approximately 3 and 2 kg/metric ton, respectively. According to Lindstrom et al. 1981, about 30% of the chlorinated matter in chlorination effluent has a molecular weight below 1000. For caustic extraction effluent is only about 5%. The amount of chlorinated organic matter with molecular weight greater than 25,000 is 10% and 55% for these two bleachery wastes, respectively. Clearly the organically bound chlorine present in compounds, sufficiently volatile to be analysable by gas chromatography, is but a small percentage of the total in bleachery wastes. Lindstrom has estimated the detectable fraction as 0.1 kg/metric ton of pulp.

Little has been published on environmental effects associated with chlorolignin. However Salkinoja - Salonen et al. 1981 have done some interesting work in Finland, where they estimate the 62 pulp mills discharge annually 20,000 tons of chlorolignin, mainly to shallow lakes or rivers. Measurements of $^{137}Cs$ levels in the sediments of three stations on a Finnish lake, which is the recipient of pulp mill wastes, were used to date the sedimentary layers. This isotope was released to the atmosphere from atomic weapons testing and the fallout peaked in 1962 to 1964. A plot of total organically bound chlorine and of chloride ion versus depth in the sediment of this lake showed that sharp increases in these parameters occurred in 1955 - the year in which the pulp mill commenced bleaching operations. The concentrations of 2,6 and 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol and tri- and tetrachlorocatechols were plotted against

sediment depth. It was concluded that less than 1% of the organically bound chlorine in the lake sediment could be acounted for as simple chlorophenols. Most of the chlorine was associated with chlorolignin which had been present in the lake sediments for periods of up to 25 years. Thus chlorolignin is very persistent in the receiving environment of Finnish lakes.

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# STUDIES IN THE DETOXIFICATION OF KRAFT MILL EFFLUENT

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Research conducted by Dr. Kutney and his co-workers in the area of microbial detoxification of kraft pulp mill effluent is long term and multifascited. The following list of publications describe the work to date.

Studies Related to Biological Detoxification of Kraft Pulp Mill Effluent. I. The Biodegradation of Dehydroabietic Acid with Mortierella isabellina. James P. Kutney, Mahatam Sigh, Gary M. Hewitt, Philip J. Salisbury, Brian R. Worth, James A. Servizi, Dennis W. Martens and Robert W. Gordon. Can. J. Chem. 59, 2334 (1981).

Studies Related to Biological Detoxification of Kraft Pulp Mill Effluent. II. The Biotransformation of Isopimanic Acid with Mortierella isabellina. James P. Kutney, Mahatam Singh, Eugene Dimitriadis, Gary M. Hewitt, Philip J. Salisbury, Brian R. Worth, James P. Servizi, Dennis W. Martens, and Robert W. Gordon. Can. J. Chem. 59, 3350 (1981).

Studies Related to Biological Detoxification of Kraft Pulp Mill Effluent. III. The Biodegradation of Abietic Acid with Martierella isabellina. James P. Kutney, Eugene Dimitriadis, Gary M. Hewitt, Mahatam Singh and Brian R. Worth. Helvetica Chimica Acta - Vol. 65, Fase. 3, p. 661-670 (1982).

Studies Related to Biological Detoxification of Kraft Pulp Mill Effluent. IV. The Biodegradation of 14-Chlorodehydroabietic Acid with Mortierella isabellina. James P. Kutney, Eugene Dimitriadis, Gary M. Hewitt, Philip J. Salisbury, Mahatam Singh, James A. Servizi, Dennis W. Martens and Robert W. Gordon. Helvetica Chemica Acta-Vol. 65, Fasc. 5, p. 1343-1350 (1982).

Studies Related to Biological Detoxification of Kraft Pulp Mill Effluent. V. The Synthesis of 12- and 14-Chlorodehydroabietic Acids and 12, 14-Dichlorodehydroabietic Acid, Fish-Toxic Diterpenes from Kraft Pulp Mill Effluent. James P. Kutney and Eugene Dimitriadis. Helevetica Chemica Acta. Vol. 65, Fasc. 5, 1351-1358 (1982).

# IN SITU MONITORING OF PULPMILL EFFLUENT USING FISH PREFERENCE/AVOIDANCE BEHAVIOUR

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## ABSTRACT

Results of a three year program to monitor the effects of sulfite mill effluent (SME) on the vertical preference/avoidance behaviour of juvenile marine fish were presented. The studies were carried out in Neroutsos Inlet, B.C. in conjunction with a pollution abatement (spent liquor recovery) program at the Port Alice sulfite mill. The in situ technique employed specially designed preference/avoidance cages which allowed juvenile fish selective access to the top 6 m of the water column. Of the different fish species tested, juvenile chum salmon (Oncorhynchus kisutch) showed the most consistent preference/avoidance response. Response time for determining avoidance in the cages was less than 0.5 h. The zone of influence defined by the preference/avoidance response initially extended to 10 km down inlet from the mill. Dissolved oxygen and pH were shown statistically to be the most significant ($p. < 0.05$) water quality variables explaining the vertical distributions observed. Monitoring during the three year study showed a reduction in the size of the SME zone of influence coincident with the mill pollution abatement program. A similar reduction in the zone of acute toxicity was also recorded. Avoidance behaviour predicted from the cage tests was observed in studies of natural fish migration patterns undertaken as part of the monitoring program. The technique was considered to be a sensitive and cost effective monitoring tool.

# EFFECTS OF KRAFT MILL EFFLUENT ON PHYTOPLANKTON AND ZOOPLANKTON

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## ABSTRACT

The plants and animals of the plankton are the base of most estuarine and marine food webs. Their capacity to escape or avoid pollutants is limited by their small size.

I have presented the results of two related plankton investigations. The first examined the joint and separate effects of chemical toxicity and shading by KME on the in situ photosynthesis of natural phytoplankton communties. The second measured the $LC_{50}$ of a typical KME for four common species of zooplankton.

We devised an incubation apparatus to hold six pairs of 250 ml bottles (one clear and one opaque for each treatment) in identical exposure at a single depth (usually 3 m) and position relative to the mill outfall (Figure 1). Natural phytoplankton assemblages from a single control source were incubated with a small addition of $H^{14}CO_3$ for about four hours. Photosynthesis was estimated as $^{14}C$ fixed. Up to four incubation moorings could be deployed in 1.5 hr from a small boat.

The typical result, repeated in general form at Crofton, Port Alberni and Powell River, is shown in Figure 2. The major effect was the suppression of Carbon fixation by shading, both at the outfall and at the 100 m downcurrent station, relative to the control site. Additions of 0.4, 2.0 and 8.0 $ml \cdot l^{-1}$ produced little effect. Commonly, there was some apparent stimulatory effect at low concentration. Partial suppression of photosynthesis occurred at higher concentrations. The lowest concentration at which we observed suppression was 20 $ml \cdot^{-1}$. This dilution (1/50) is achieved by most well-designed outfalls within a few tens of meters from discharge.

In the second study, we performed standard 96-hour $LC_{50}$ experiments on the herbivorous copepods Calanus marshallae and Mertridia pacifica, and the predatory copepods Tortanus discaudatus and Epilabidocera longipedata. We presented salt-balanced KME in natural seawater at 0%, 1%, 5%, 10% and 15%. The survival of the control herbivores was better than that of the carnivores. The 96 hr $LC_{50}$ for the hardiest of the four species, Calanus marshallae, was 12% of an effluent which routinely gave $LC_{50}$ greater than 25% for juvenile salmonids (Figure 3).

The effect of KME on phytoplankton appears to be caused mostly by shading, to be confined to the immediate vicinity of the outfall, and to be reversible by transport to clearer water.

Copepods, the commonest zooplankters, are more sensitive to KME than are juvenile salmonids.

## ACKNOWLEDGEMENTS

I thank Dr. Jack L. Littlepage of the University of Victoria for his participation in the phytoplankton work, which was supported by the Cooperative Pollution Abatement Research Program. Jane M. Koleba performed the zooplankton experiments on a summer student subsidy from the Province of British Columbia. She and I were then employed by Dobrocky Seatech Ltd., Victoria, B.C.

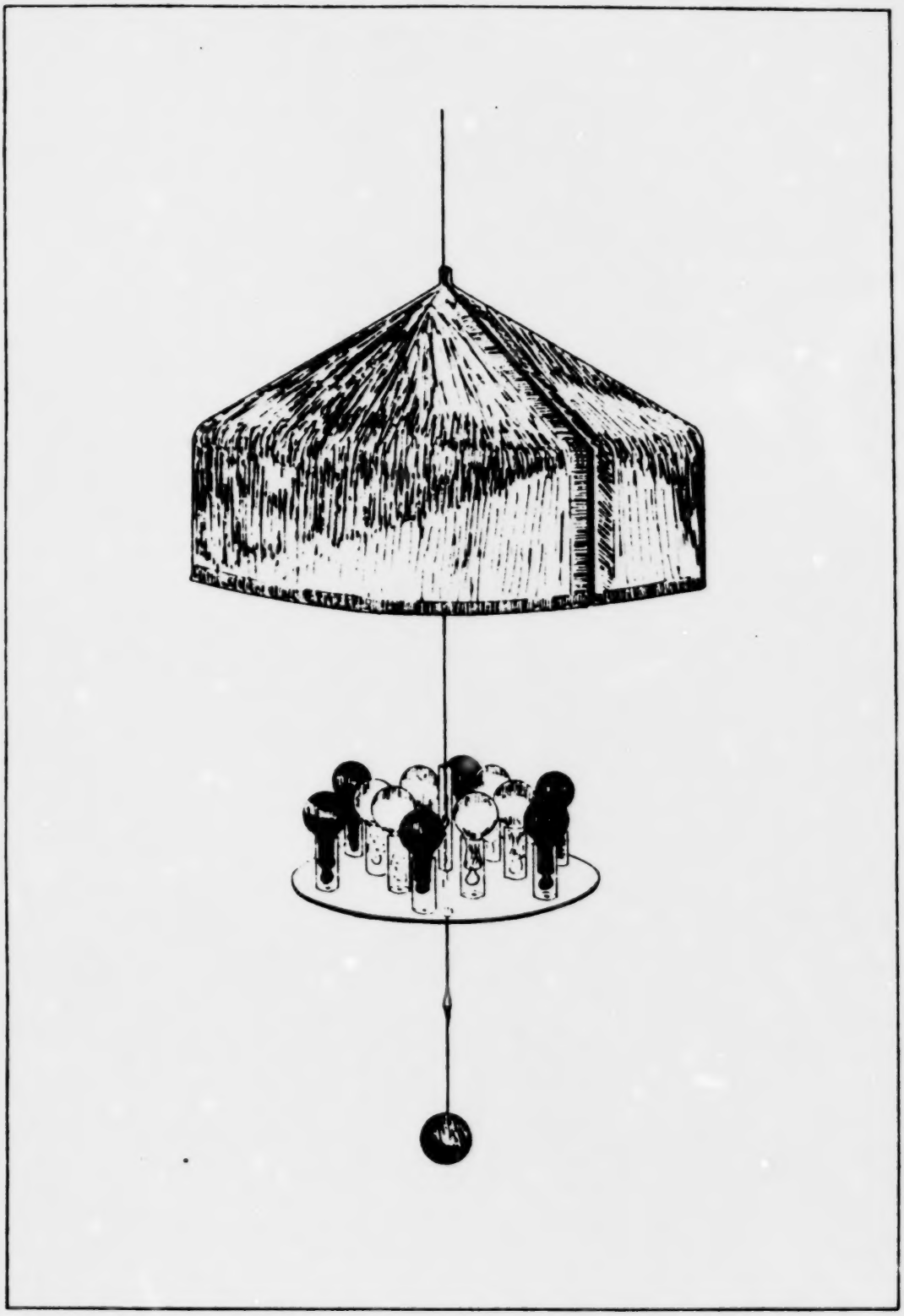

Figure 1. Incubation disc with hood.

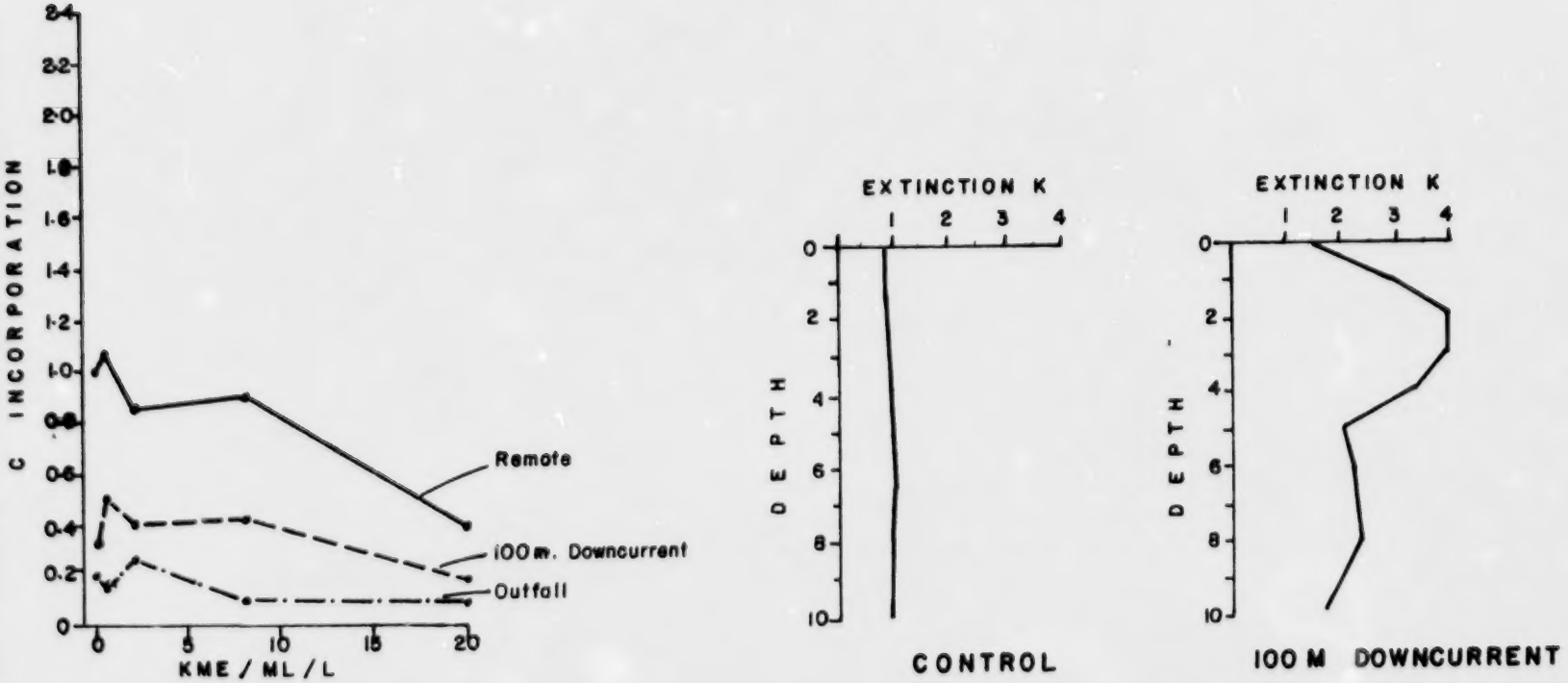


FIGURE 2 PHYTOPLANKTON EXPERIMENT 2: In situ CARBON FIXATION VERSUS KME CONCENTRATION AND DOWNCURRENT DISTANCE FROM A TYPICAL COASTAL PULP MILL OUTFALL

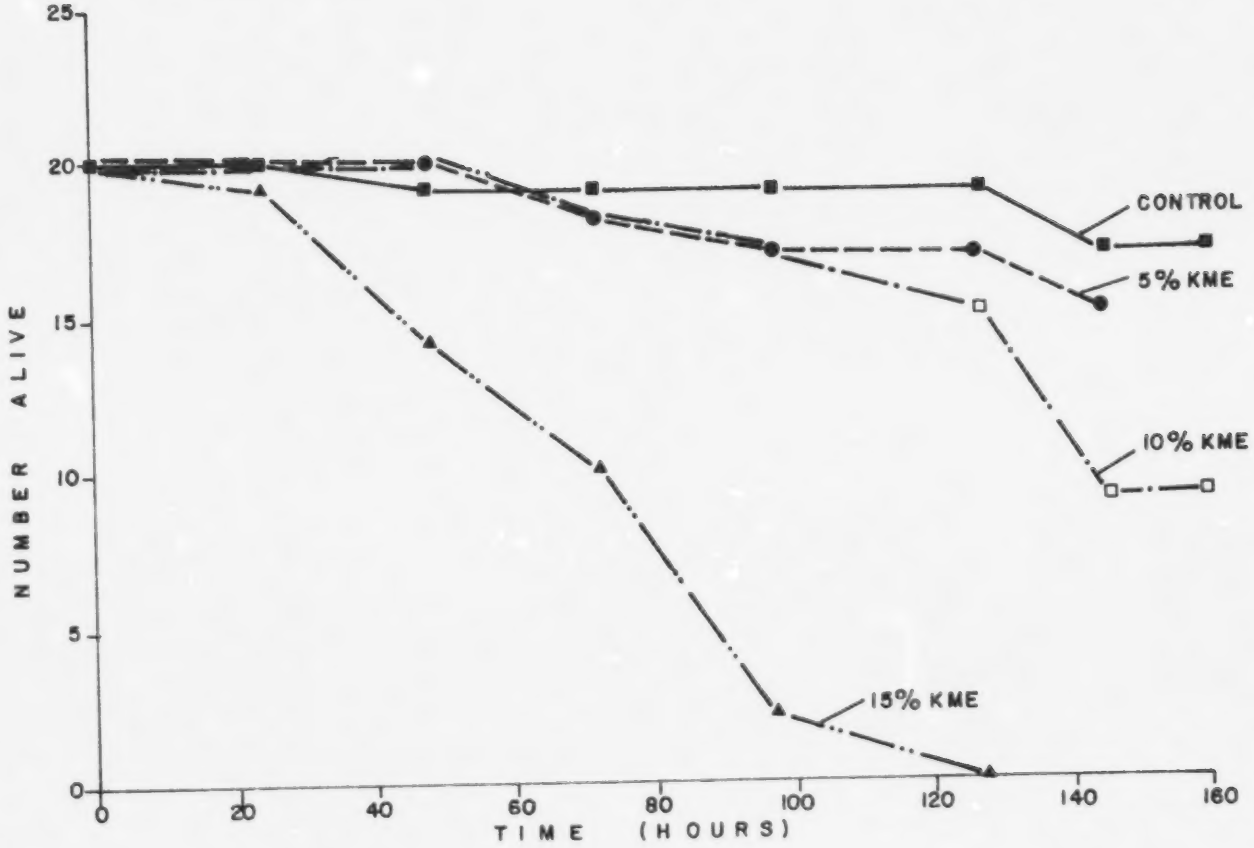


FIGURE 3 COMBINED RESULTS OF EXPERIMENTS 5 AND 6: SURVIVAL OF *Calanus pacificus* in 5%, 10% AND 15% SALT-BALANCED KME

# USE OF MUSSELS AS SENTINEL ORGANISMS IN MONITORING WATER QUALITY: A MULTIVARIATE STATISTICAL APPROACH

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ABSTRACT

A significant problem in the use of mussels as sentinel organisms for monitoring trace metals is that the body burden of these substances in the mussels is dependent upon other variables besides their concentration in the marine environment. Two of the more obvious, extraneous variables are body size of the mussels and the time of year collection. Hence, one procedure for extracting out the relevant data is to apply multi-variate analysis. To this end a principle component analysis was applied to the correlation matrix of metal concentrations and other variates such as body size of mussels collected from a reference area assumed to have low inputs of trace metals. Three principal components were extracted from the matrix and two of these were used to calculate "principal component scores" for the mussels not only from the reference area but for others as well. The magnitude of the score can be used to indicate how well any individual mussel resembles an "average" mussel from the reference area. A large score means that the mussel in question has only a low probability of resembling the "average" mussel from the reference area. The statistical technique described here provides an inexpensive method for monitoring using just a few mussels from each area.

# POLYCHAETES RECORDED NEAR TWO PULP MILLS ON THE COAST OF NORTHERN BRITISH COLUMBIA: A PRELIMINARY TAXOMONIC AND ECOLOGICAL ACCOUNT

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ABSTRACT

Two locations on the coast of northern British Columbia were sampled during the years 1972 to 1975 in an attempt to determine the long term effects of pulp mill wood waste on marine benthic communities. Industrial activity at Swanson Bay ceased about 1935, but Cousins Inlet was still receiving wastes from a groundwood plant in 1975. Polychaetous annelids were dominant in most samples from both locations.

Dissolved oxygen in the bottom waters of Cousins Inlet were much improved when compared with previous surveys made in 1962 when a sulfate and sulfite mill was operating. Natural sediments in Ocean Falls Harbour at the head of the inlet were completely covered with wood chips, fibers and paper waste. Ninety-one species of polychaetes were identified in 26 samples from eight stations, with stations near the mouth of the fjord being most productive and those in the harbour virtually barren.

Bottom oxygen in Swanson Bay was much higher than in Cousins Inlet, due to strong tidal currents in Graham Reach. Wood waste was well mixed with natural sediments (sand, shell, gravel). Eight samples from two stations yielded 126 species of polychaetes, indicating that the infauna of such channels may be among the most diverse benthic polychaete communities recorded.

Of the 166 taxa of polychaetes collected from these two locations, 34 appear to be new to British Columbia, and six may be new to

science. Certain new records may be due to introductions from ship traffic, especially Pionosyllis uraga Imajima (Syllidae) from Japan, and Tharyx tessalata Hartman (Cirratulidae) from California.

# THE FUCUS-EPIFAUNAL COMMUNITY: A MULTVARIATE APPROACH TO MONITORING THE EFFECTS OF PULPMILL EFFLUENT DISCHARGES

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ABSTRACT

Analysis of the macroinvertebrates associated with the common 'rockweed' Fucus was shown to provide an effective community-based biological technique for monitoring displacements in shoreline ecosystem structure and function as a result of pulpmill effluent discharges.

Fucus samples taken at 107 shoreline sites around Vancouver Island, and along the British Columbia mainland coast, revealed the natural variation within the 25 invertebrate species comprising this algal community. Using non-centered Principal Components Analysis (PCA) and Polar Ordination (PO) procedures, variation within the 'normal' community was related to the degree to which the sampling site was exposed to wave or current action. In all cases, similarity of Fucus community structure (as measured by species composition and numerical contribution) between 'normal' sites and those sampled in the vicinity of pulpmill discharges, was directly proportional to distance from the waste source. Community responses due to changes in natural enviornmental parameters (e.g., salinity) were differentiated from pollutant effects by correlating species richness with a measure of numerical dominance. In regions influenced by pulping effluents dominance increased significantly with decreased species richness, in response to the imposed waste. Natural environmental variation supported the converse relationship.

This technique was successfully tested in an environmental rehabilitation assessment. Fucus samples taken both prior to and after implementation of pollution controls restricting the discharge of process

wastes from the Port Alice sulfite-based pulpmill, illustrated a significant biological recovery within the Fucus communities at sites previously affected by the discharged pulping wastes. This recovery was correlated with water quality improvements observed over this period.

Overall, the Fucus-epifauna survey was shown to be an effective distribution-based biomonitoring technique. Using all of the macroinvertebrates associated with Fucus provides an array of species characteristic of several taxomonic groups revealing differential sensitivies to a pollutional stress such as pulping effluent. In addition, considering changes in community structure in a distribution-based method will reflect interactions between both abiotic and biotic factors. More important, accurate documentation of community structural differences will provide information on possible functional changes due directly or indirectly to pollution effects.

The multivariate statistical approach used in this study reduces the multidimensionality of the Fucus community structural data. Non-centered PCA is considered particularly effective in pollution assessments in that community irregulatities, evident as sample disjunctions within the data matrix, are clearly differentiated from communities representative of undistrubed environments. Additionally, graphical presentation of ordinated, disturbed Fucus-epifaunal community samples with an appropriate group of samples characteristic of normal habitats can visually communicate information on the extent and/or rate of impact or recovery within a geographical range.

# ENVIRONMENTAL IMPACTS OF BOTTOM DEPOSITS ORIGINATING FROM B.C. COASTAL PULP MILLS: A GENERAL SUMMARY

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## ABSTRACT

Pulp mills release several thousand Kg per day of suspended solids in their effluent to the marine environment. A large portion of the discharged effluent consists of wood fibres which can settle out impacting on the receiving environment. Direct removal of bottom habitat and organisms by smothering with decomposing deposits up to several metres in thickness and the creation, in some areas, of zones of low dissolved oxygen concentration close to the bottom are two of the most obvious impacts. The degree to which these occur increases with decreasing circulation and water exchange rates. Studies to date indicate habitat recovery following termination of pulp mill operation to be a long process requiring a combination of fibre decomposition and covering by natural sediments before recolonization by flora and fauna occurs to any great extent. In addition to habitat removal, fibre deposits also contain toxic substances such as resin acids and associated breakdown products which may control species distribution and result in bioaccumulation in areas of fibre deposit.

## INTRODUCTION

The coast of British Columbia has 11 pulp and paper mills discharging to the marine environment (Figure 1). These release high levels of BOD and total suspended solids (TSS) in their effluent each day. The amount, often in excess of provincial permits, is dependent upon individual mill processes, production levels and pollution abatement

programs/equipment. Daily averages of TSS in 1981 ranged from 8.14 tonnes at Port Mellon to 39.97 tonnes at Woodfibre (Table 1). The settleable portion of the TSS - fibre, mud, etc., - are, based on preliminary information and field observations, believed to form flocs on contact with saline waters. Settlement of these to the bottom in areas adjacent to the mills results in the formation of anoxic deposits.

As part of its regular surveillance monitoring program, EPS attempts to conduct yearly receiving environment studies at all pulp mills on the B.C. coast. In this presentation, I will be discussing the mills at Prince Rupert, Ocean Falls, Harmac and Woodfibre. Factors believed to be controlling the location and extent of fibre deposits will be discussed. Published reports by EPS are available on these and other mills as listed in the bibliography.

To effectively study mill impact, EPS has been employing standard oceanographic - water quality and benthic ecology techniques using surface/ship deployed equipment. Direct visual observations of the benthic environment were also made using the three man PISCES IV submersible. Surface deployed samplers alone do not provide a complete picture of the nature of benthic impact. The PISCES has shown that the surface of the deposits are so unconsolidated that they are not effectively sampled by grabs, etc. Samples have been obtained with the PISCES to determine the make-up of the deposit surface.

## SUMMARY OF BENTHIC IMPACTS

Typical marine near shore subtidal substrates for the coast of B.C. consist of sand/silt sediments of various degrees of consolidation. Buildup of organic debris and the presence of reducing sediments are atypical in most areas. Site specific activities such as log booming and storage result in large amounts of wood/bark debris on the bottom. Reducing sediments occur in these immediate areas. Other areas of high organic input are domestic sewage outfalls. Sediments in these receiving

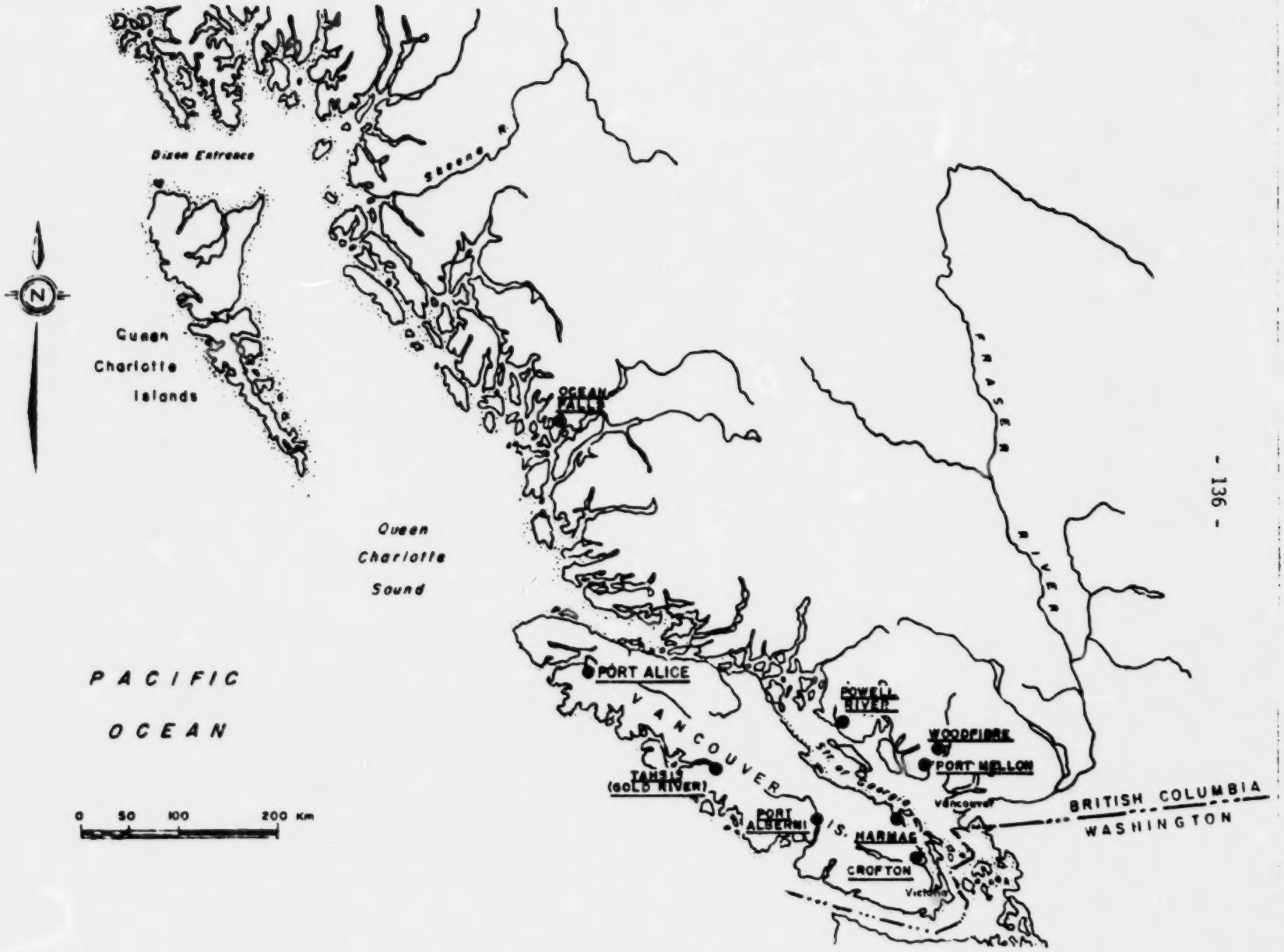


FIGURE 1 LOCATION OF COASTAL PULPMILLS

TABLE 1.

YEARLY AVERAGES FOR BOD AND TSS FROM B.C. PULP AND PAPER MILLS

| NAME OF MILL | 1975 | | 1980 | | 1981 | | 1981 Provincial Allowances for | |
|---|---|---|---|---|---|---|---|---|
| | BOD ton/day | TSS ton/day | BOD ton/day | TSS ton/day | BOD ton/day | TSS ton/day | BOD | TSS |
| **COASTAL MILLS** | | | | | | | | |
| BCFP LTD., CROFTON PULP & PAPER DIV. | 46.53 | 41.10 | 53.51 | 22.63 | 52.29 | 19.02 | 46.60 | 23.80 |
| B.C. TIMBER, SKEENA PULP DIV. | 341.85 | 67.88 | 33.48 | 22.22 | 35.60 | 22.15 | 33.50 | 19.70 |
| CFP LTD., HOWE SOUND PULP DIV. | 10.24 | 22.47 | 13.81 | 10.33 | 15.09 | 8.14 | 17.40 | 10.15 |
| CR. ZELLERBACH CAN. LTD., ELK FALLS MILL | 50.37 | 30.02 | 41.10 | 21.25 | 36.69 | 22.01 | 43.50 | 29.00 |
| M&B LTD., ALBERNI PULP & PAPER DIV. | 13.61 | 13.21 | 13.55 | 22.48 | 17.14 | 17.26 | 23.15 | 13.23 |
| M&B LTD., HARMAC PULP DIV. | 28.26 | 13.98 | 20.62 | 13.22 | 26.02 | 13.31 | 27.00 | 12.00 |
| M&B LTD., POWELL RIVER DIV. | 30.60 | 63.19 | 28.93 | 27.03 | 33.52 | 31.11 | 44.50 | 30.50 |
| OCEAN FALLS CORP. | 2.00 | 9.43 | 3.62 | 12.29 | Closed | Closed | Closed | Closed |
| TAHSIS CO. LTD., GOLD R. PULP MILL | 14.10 | 19.72 | 14.87 | 9.26 | 13.38 | 14.98 | 25.30 | 13.30 |
| WESTERN FOREST PROD., PORT ALICE DIV. | 205.25 | 27.94 | 81.57 | 24.41 | 68.83 | 24.32 | 75.40 | 8.45 |
| WESTERN FOREST PROD., WOODFIBRE DIV. | 12.19 | 29.94 | 14.93 | 45.65 | 18.66 | 39.97 | 18.27 | 9.56 |

environments are generally similar in appearance to 'normal' sediments aside from an accumulation of plastics etc. A limited zone (100-200 m) of reducing sediments may also exist (Pomeroy 1981).

Pulp mills, also sources of high organic input to the sea, often have a much more extensive and serious zone of influence compared to the above mentioned. Reducing deposits of mill origin have been noted several kilometres from the point of mill discharge at some locations, while at others, deposits tend to be much more restricted. Examples are discussed below. More complete information can be found in the indicated report.

Ocean Falls (Packman 1979)

This is an excellent example of an area showing severe environmental impact due to fibre deposition. The mill has operated to varying levels since 1912 until closure in July of 1981 (Packman 1979).

Ocean Falls is located at the head of Cousins Inlet which has limited freshwater input and low marine exchange rates. Since start up, effluent from the mill was surface discharged into the tailrace of the hydro electric dam on the Link River beside the mill. TSS discharge of about 9-12 tonnes/day were recorded when the mill was operational.

Two main areas of impact were evident in Cousins Inlet from the Ocean Falls mill.

Water Quality. Extremely low dissolved oxygen values were recorded near the bottom for some distance from the mill. In 1962 levels were less than 1.0 mg/l near the mill, rising to greater than 1.5 mg/l in 1974 after chemical pulping was stopped. Since 1974, dissolved oxygen levels have continued to increase, reaching 4-5 mg/l at the bottom in 1981. General water quality is sufficiently improved at this point to permit a sable-fish farming operation to move into the inlet. Even greater improvement is expected following mill closure.

Benthic Habitat. The removal of benthic habitat has been a much more extensive and longer term problem. During the 69 years of operation, a significant deposit has resulted up to 3.5 km from the mill (Figure 2). Adjacent to the mill itself, the deposit was estimated to approximately 15 m thick, decreasing to isolated thin patches in a 'transition zone' extending an additional 1.3 km, for a total impact distance of some 4.8 km.

In the heavy benthic impact zone, the deposit is strongly reducing, with bubbles of $H_2S$ gas being released and portions of the deposit being brought to the water surface by gas accumulation. The deposit itself appeared in the 1976 PISCES dive as a thick layer of black reduced fibre (etc.) overlain with about 1.5 to 2.0 cm of newly deposited material. The latter appeared white, presumably due to the presence of fibres and bacterial growth. The deposit was extremely unconsolidated with shock waves being transmitted easily.

No obvious life was present in this area aside from sea anemones on logs projecting from the deposit. The latter contained numerous species of polychaete worms, especially capitellids which are characteristic of high organic deposit areas. Small fish, sole and shrimp appeared with increasing distance from the mill.

Considerably more life was evident to the 'transition zone' where the substrate consisted of a brown detrital/sediment layer over black $H_2S$ ooze. Patches of black reducing sediment were present with a surface cover of white as in the high impact total cover area. Benthic fauna were abundant with seapens dominant at about $50/m^2$.

Increases in organic content and certain heavy metals in the sediments were evident with proximity to the mill (Table 2). Zinc for example increased from 112 ppm to near the mouth of Cousins Inlet to near 700 ppm close to the mill.

Natural rehbilitation/recolonization of the alienated benthic habitat is going to be a slow process at Ocean Falls. Due to the restricted input of sediments from rivers and the limited contribution

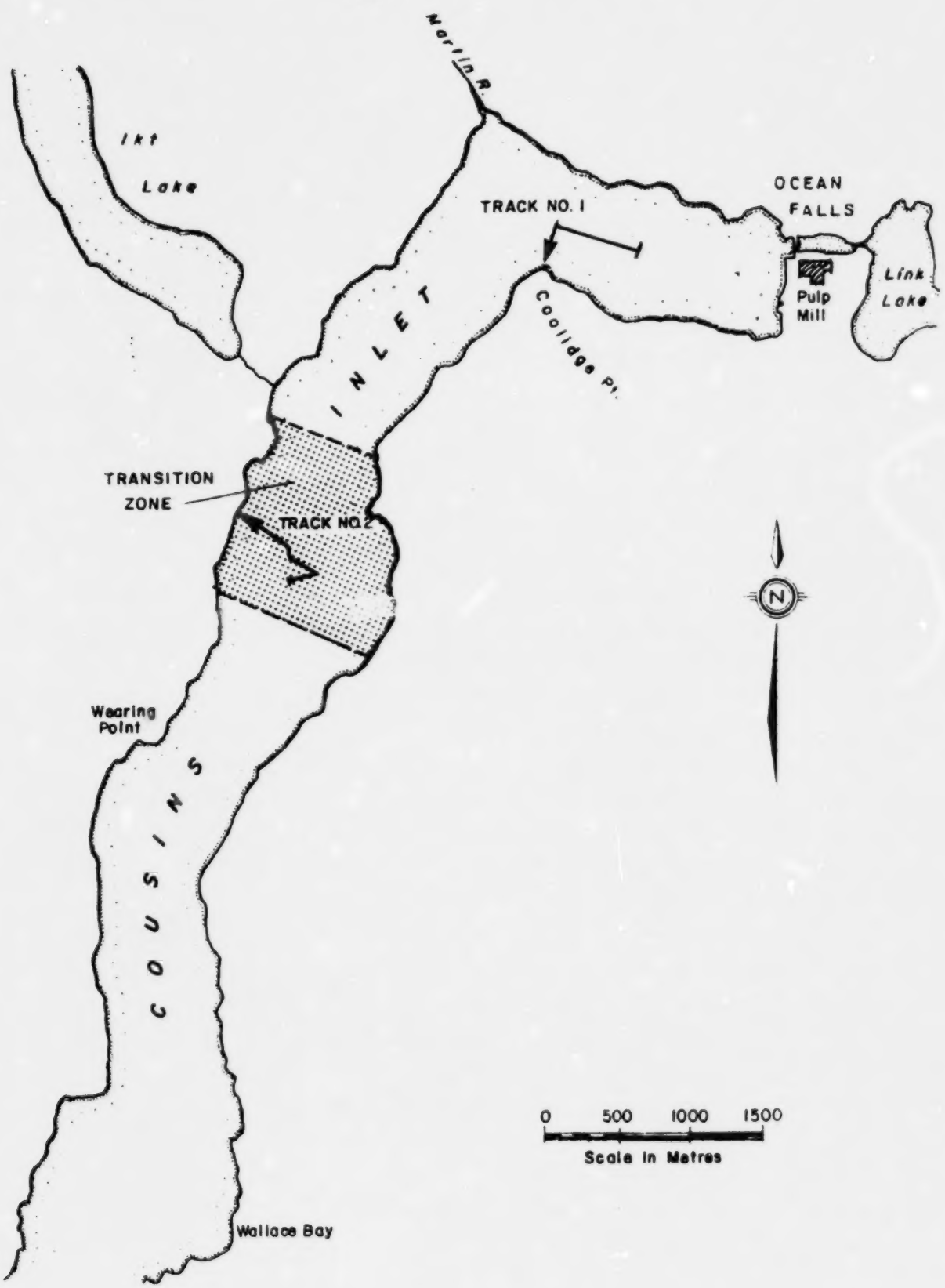


FIGURE 2 PISCES IV DIVE TRACKS AT OCEAN FALLS

TABLE 2. OCEAN FALLS: SUBSTRATE HEAVY METALS AND ORGANIC CONTENT

| STN. | ORGANIC TVR (%) | HEAVY METAL Hg (ppm) | Zn (ppm) | Cu (ppm) | Pb (ppm) | Cd (ppm) |
|---|---|---|---|---|---|---|
| 4a | 18 | 0.33 | 112 | 70 | 17 | 1.0 |
| 5 | 25 | 0.36 | 130 | 50 | 19 | 1.5 |
| 12 | 48 | 0.40 | 445 | 52 | 27 | 2.0 |
| 13 | 56 | 0.55 | 620 | 119 | 39 | 3.1 |

from the sea, covering or capping of the deposit will take many years. The highly embayed nature of the inlet and the slow water exchange rates favored extensive deposit formation and now deter benthic habitat recovery rates.

Woodfibre (Nelson, 1979)

Effluent discharge from the Woodfibre pulp mill has resulted in extensive environmental impact similar to that seen at Ocean Falls.

Woodfibre is located inside a sill in Howe Sound, a true fjord receiving glacial melt waters via the Squamish River. The area is characteristic of a salt-wedge estuary where the seaward flow of river water is replaced by a compensatory sub-surface current flowing up the sound. The sill inhibits the entry of deep waters from outside. This feature results in naturally low dissolved oxygen in bottom waters behind the sill in the area of the pulp mill.

The Woodfibre pulp mill was opened in 1912 and currently runs as a bleached sulphate (kraft) mill. Effluent is discharged into a creek by the mill and subsequently into the surface waters of Howe Sound. No fibre recovery systems are operated with the result that an estimated average of 39.97 tonnes/day TSS went out in the effluent in 1981. Permitted levels are 9.56 tonnes/day.

The general appearance of the fibre deposit and the types of benthic impact at Woodfibre are quite similar to those noted for Ocean Falls. PISCES dives made in 1979 and 1982 indicated an extensive deposit extending out from the mill about 1 to 1½ km (Figure 3). Close to the mill, the deposit was identical in appearance to that adjacent to Ocean Falls. Flocculated fibre material (etc.) was seen cascading down the steep slopes off the Woodfibre mill. Sole, shrimp and some crabs were evident on the deposit itself and anemones on rocks to about 150 m indicating the presence of sufficient oxygen in the waters above the undisturbed deposit. Beyond this depth to the bottom at 250 m, the deposit became less obvious, appearing brown in colour. A slower rate of

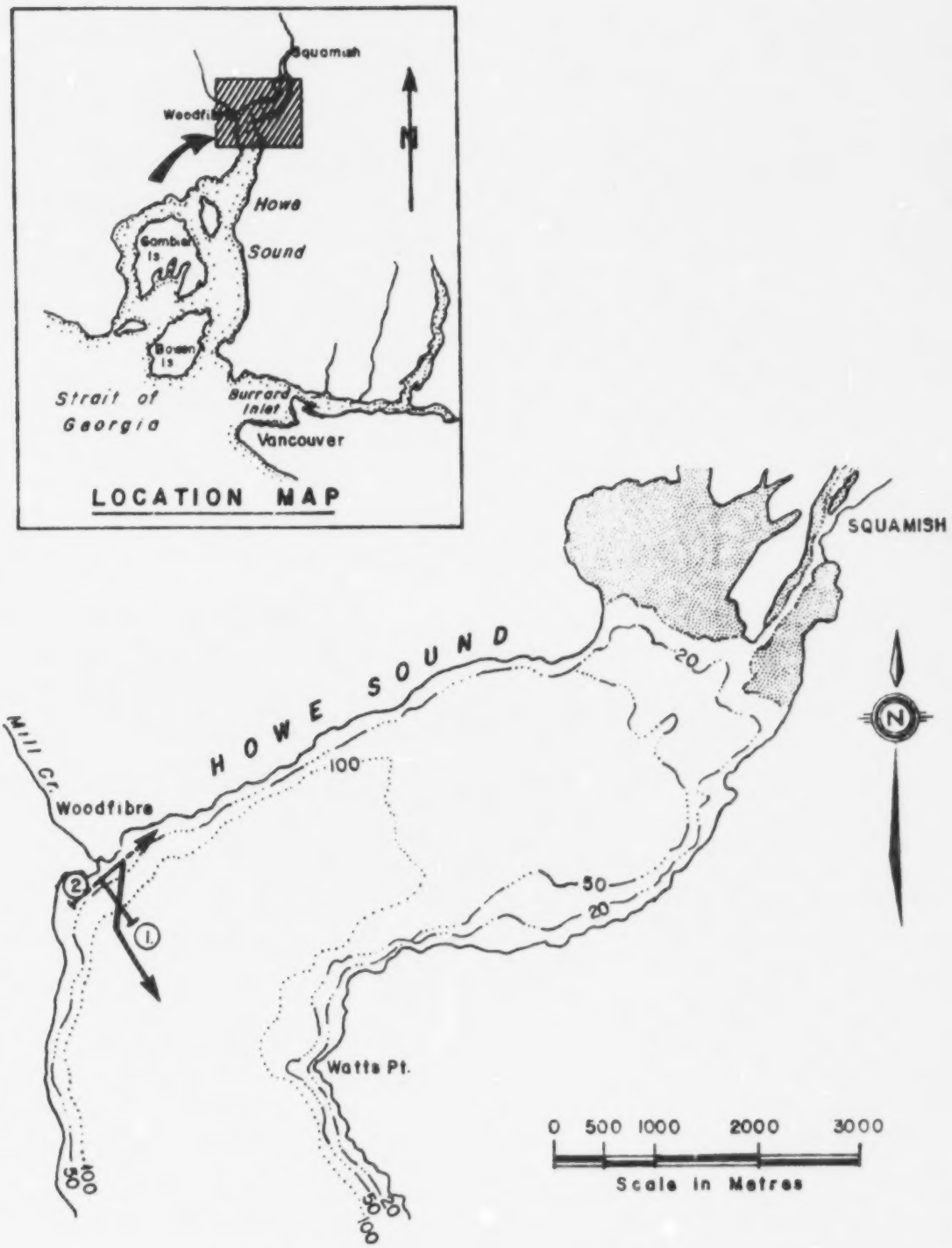


FIG. 3 PISCES DIVE TRACKS, WOODFIBRE (1979).

fibre deposition was apparent and the region could be termed transitional. The sediments were devoid of life reflecting the absence of oxygen. The contribution of mill effluent to this anaerobic condition is difficult to determine due to naturally low oxygen in the deep waters adjacent to the mill.

Samples of deposit obtained from Woodfibre in 1982 had levels and species of resin acids suggesting its pulpmill origin (isopimaric acid at 0.03 mg/g and dehydroabietic at 0.03 mg/g dry weight).

At Woodfibre, the high TSS input, rapid flocculation on entering the marine environment and 'trapping' due to the salt-wedge nature of the sound; ll contribute to fibre bed formation.

Harmac (Packman, 1978)

Fibre deposit formation in the tidally influenced Northumberland Channel off the Harmac pulp mill is in its early stages. Installation of a submarine diffuser 105 m deep in 1976 removed effluent from a surface shoreline discharge operating since mill opening in 1950 releasing it to the centre of Northumberland Channel. Recovery of shoreline biotic communities has been recorded since 1976.

The Harmac mill is considered to have good in-plant effluent control systems. Currently a daily average of 13.31 tonnes/day TSS and 26.02 tonnes/day BOD are released, approaching provincial permit allowances. Water circulation in Northumberland Channel results in rapid dilution of the effluent to the point where no significant water quality problems have been identified. No depressed bottom dissolved oxygen levels have been noted. Due to the density stratification of the channel, the discharged effluent is trapped before it enters surface waters.

A PISCES dive in 1978 indicated that a fibre deposit was beginning to form near the end of the diffuser, two years after start-up. Further dives in 1981 revealed the existence of an extensive deposit in the centre of Northumberland Channel (Figure 4). The deposit was a 'miniature' of the Ocean Falls situation with heavy deposit, high impact

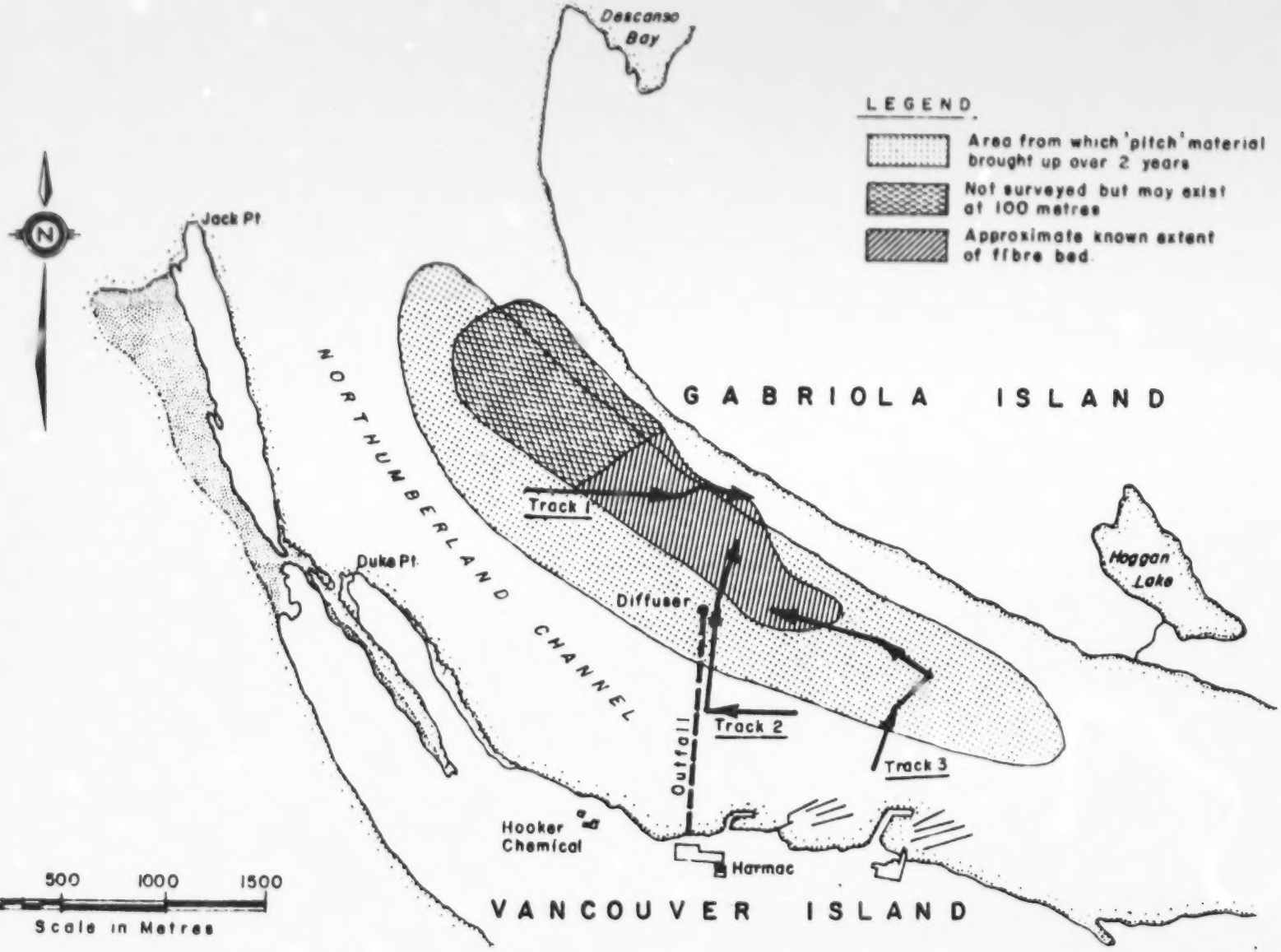


FIG. 4 DIVE TRACKS AND FIBRE BED EXTENT (HARMAC - February 25-26, 1981)

areas identified closer to Gabriola Island and lower deposit, 'transition zones' nearer the mill side of the channel. Texture, gross appearance and response of the deposit to disturbance (ie., shock waves) were similar to conditions at Woodfibre and Ocean Falls. The impact of habitat removal was obvious with only a few shrimp, sole and crabs noted on the surface of the deposit and anemones on projecting rocks and logs. Polychaete worms were present in the deposit as was the case at Ocean Falls. Fauna increased in abundance in the low impact area and again where no accumulations of deposit were noted. A 1982 dive has shown the deposit to be increasing in extent.

The area in Northumberland Channel below about 80 m appears to be functioning as a 'sink' for TSS in the mill effluent. On entering the saline waters, the material (fibres, mud, etc.) flocculates and traps. Sub-surface circulation patterns and currents appear to be such that the material settles.

Prince Rupert (Packman, 1979)

The B.C. Timber mill at Prince Rupert was opened in 1950 as a bleached sulphite mill, converting to all kraft production by 1978. Until 1976, Wainwright Basin received high inputs of TSS in mill effluent. Dissolved oxygen in the water column reached near zero due to very low flushing rates of the Basin. Large intertidal and subtidal fibre deposits formed by 1966. Benthic fauna was virtually non existant and intertidally restricted to some worms, crustaceans and poorly developed algae. Large mats of fibre frequently appeared on the surface, raised by $H_2S$ gas accumulation as at Ocean Falls. Intertidal habitat and water quality recovery occurred quite quickly once effluent discharge was diverted to Porpoise Harbour in 1978.

The mill has been operating without a clarifier, discharging via a diffuser in 18 m of water (Figure 5). EPS identified a fibre deposit in 1980/81 forming in the vicinity of the diffuser in response to an average daily discharge of about 22 tonnes TSS. The pattern of deposition and

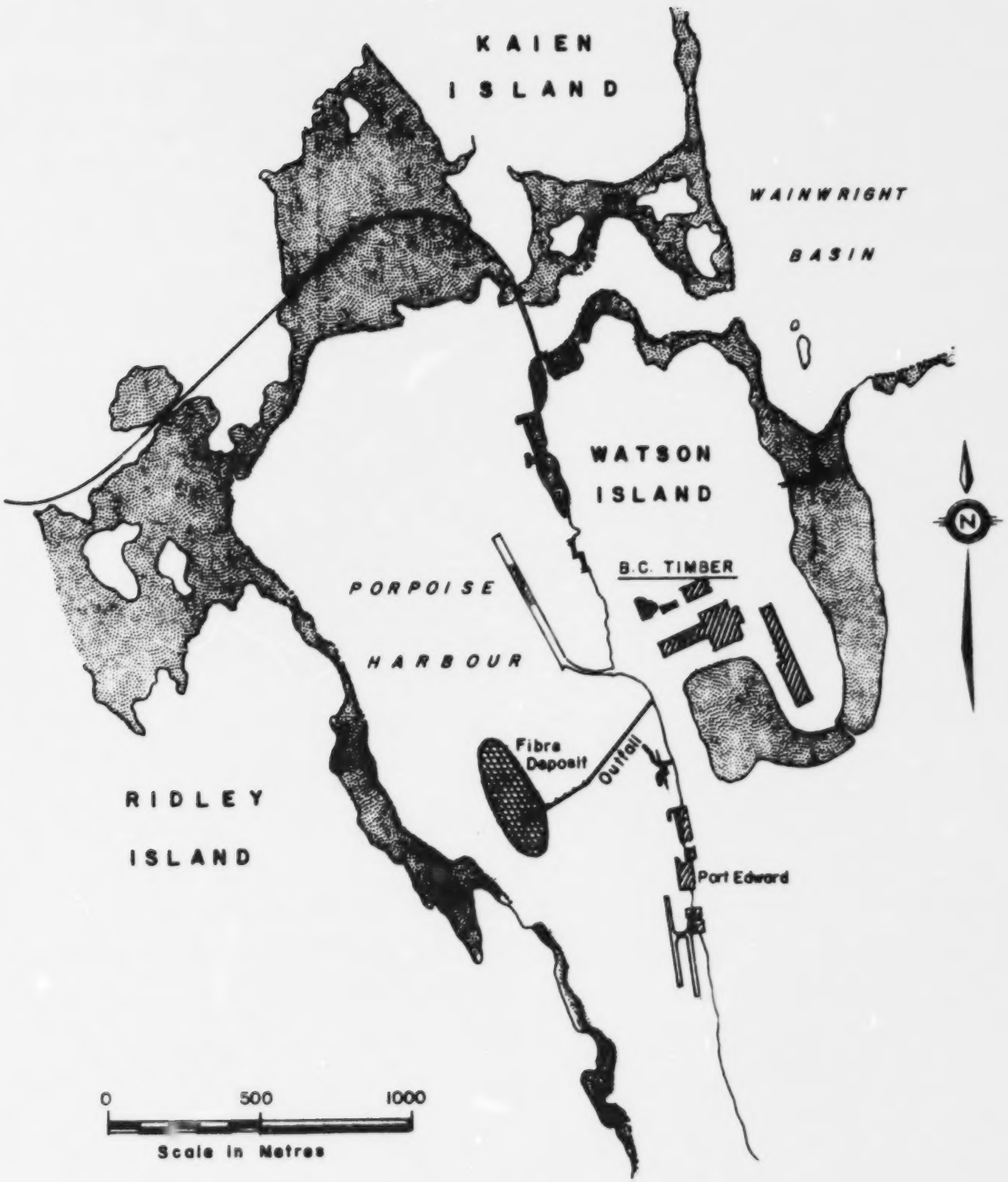


FIGURE 5 ESTIMATED FIBRE DEPOSIT EXTENT AT PRINCE RUPERT

benthic impact of this deposit has not yet been determined. It appears that a concentrating mechanism is operating similar to Harmac, depositing fibre in the deeper parts of the Harbour.

EPS PULPMILL REPORTS

| Regional Program Report # | Title/Author |
|---|---|
| 79-2 | Pulp Mill Environmental Impact Assessment<br>Canadian Forest Products Limited, Howe Sound Pulp Division.<br>H. Nelson |
| 79-3 | Pulp Mill Environmental Impact Assessment<br>Rayonier Canada Limited, Woodfibre, B.C.<br>H. Nelson |
| 79-4 | Pulp Mill Environmental Impact Assessment<br>Tahsis Company Limited, Gold River, B.C.<br>D.L. Sullivan, H. Nelson |
| 79-5 | Pulp Mill Environmental Impact Assessment<br>B.C. Forest Products, Crofton Pulp & Paper Division.<br>H. Nelson |
| 79-6 | Pulp Mill Environmental Impact Assessment<br>Ocean Falls Corporation, Ocean Falls, B.C.<br>G.A. Packman |
| 79-7 | Pulp Mill Environmental Impact Assessment<br>Canadian Cellulose Limited, Northern Pulp Operations, Port Edward, B.C.<br>G.A. Packman |
| 79-8 | Pulp Mill Environmental Assessment<br>MacMillan Bloedel Co. Ltd., Harmac Pulp Division.<br>G.A. Packman |
| 79-9 | Pulp Mill Environmental Assessment<br>Crown Zellerbach, Elk Falls Mill.<br>G.A. Packman |
| 79-10 | Marine Environmental Surveillance of Muchalat Inlet, B.C. 1976-77.<br>D.L. Sullivan |
| 79-11 | Pulp Mill Environmental Assessment<br>MacMillan Bloedel Co. Limited, Alberni Pulp & Paper Division.<br>H. Nelson |

# THE BACTERIAL SULPHURETUM: DOES IT EXIST AT HARMAC?

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ABSTRACT

The seabed in Northumberland Channel adjacent to the submarine outfall of the Harmac Mill supports at the water column interface a mat of filamentous material tentatively identified as a form of the sulphide oxidizing bacterium Beggiatoa. Such mats are known to form on the seabed as part of organically enriched, e.g. cellulose-metabolising and other (often natural), ecosystems (sulphureta). At one marine discharging pulp mill, the sulphuretum is known to have come into a state of equilibrium with the effluent discharge, with a net export of nutrients released to the water column from the sediment. Northumberland Channel is now being investigated to determine the extent of the bacterial mat, and its spatial relationship with benthic species associations.

## 1. INTRODUCTION

On February 25 and 26, 1981 during submersible dives, members of the Environmental Protection Service recorded a soft, white "fibre" deposit of uncertain thickness on the seabed in Northumberland Channel. It extended from near the submarine outfall of the Harmac pulp mill towards Gabriola Island. This was reported by in-house memorandum (M. Pomeroy and L. Harding, personal communications) with a tentative distribution map, and notes on organisms and materials present, and texture. The survey had been initiated by complaints from fishermen, that trawls in the area were collecting aggregates of pitch-like material, sediment and fibre. A sample analysed was toxic to rainbow trout giving a 96 $LT_{50}$ of 20-24 hours at 4.2% by volume, and contained wood derivatives (tetrahydropimaric acid, a diterpene hydrocarbon, and wood sterols) suggested by the analyst as having arisen from resin acids (by the bacterial breakdown of wood material under anaerobic conditions).

Following the dives, the Geological Survey made a high resolution sonar transect through Northumberland Channel, and took sediment samples for analysis (M. Pomeroy, personal communication). Environmental staff of MacMillan Bloedel Ltd. also took a set of sediment samples for analysis (R. Young, personal communication). The nature of the white "fibre" deposit remained uncertain due to difficulties in obtaining samples. Late in 1981, the University of Victoria (D.V. Ellis) was requested by MacMillan Bloedel Ltd. to initiate investigations of the seabed and its biology. Layout of the various sampling stations and dives to 1982 is shown in Figure 1, and a summary of surveys in Table 1.

## 2. THE UNIVERSITY INVESTIGATION TO DATE

The university group made a series of dives with the submersible Pisces (Figure 1), and took benthic samples by otter trawl, Craib corer and 0.1 $m^2$ Van Veen grab during August 31 - September 3, 1982.

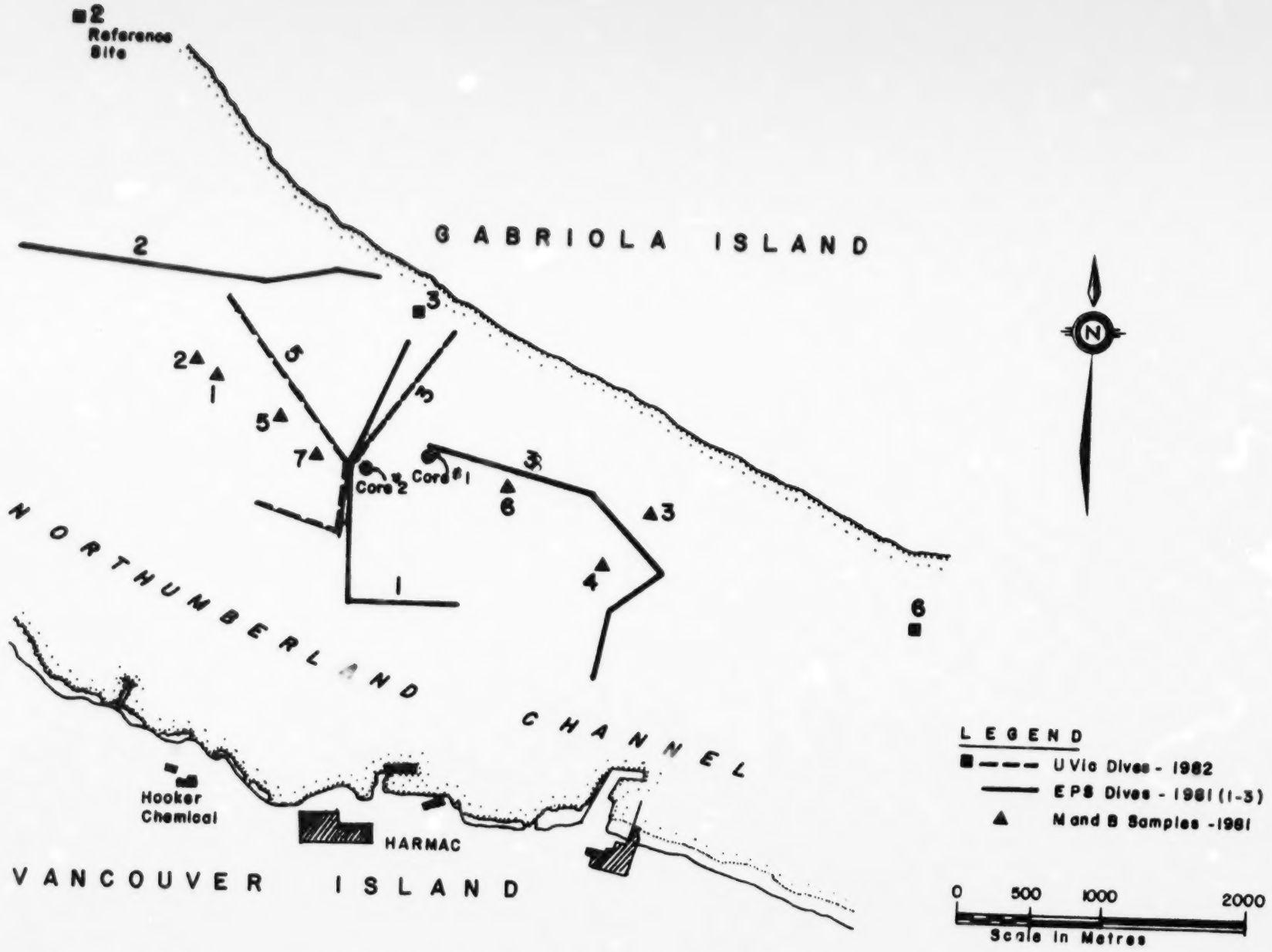


FIGURE 1 PISCES DIVE TRACKS AND BENTHIC SAMPLE STATIONS - 1981 - 1982

TABLE 1 SURVEYS IN NORTHUMBERLAND CHANNEL 1981-83

| DATE | AGENCY | TYPE | RESULTS |
|---|---|---|---|
| 1981 | | | |
| Feb. 25, 26 | Environmental Protection Service | Submersible | White "fibre" deposit recorded.<br>Depauperate benthos noted.<br>Samples - wood derivatives<br>- toxic |
| April 7 | Geological Survey | High resolution sonar samples<br>Cores | Deposit not recorded on sonar trace.<br>Suggestions of methan gas pockets (by J. Luternauer, Geological Survey of Canada).<br>0-1 cm organics 17.6%.<br>>1 cm organics 3.9-8.0%. |
| April 19 | MacMillan Bloedel Ltd. | Water samples<br>Cores<br>UW photos | Some wood derived materials.<br>Fungal cultures negative. |
| 1982 | | | |
| Aug. 31 - Sept. 3 | University of Victoria | Submersible<br>Benthos<br>Cores | White mat recorded.<br>Depauperate benthos recorded.<br>Mat sampled and organisms cultured. |
| 1983 | | | |
| March 15-17 | University of Victoria | Submersible | White mat mapped.<br>Benthos transects quantified. |

Layout of the grab stations now reported is shown in Figure 2 and was along the line of the university submersible dives 1 and 2 (Figure 1). The white deposit was recorded in approximately the same position as during the earlier dives, but was possibly less extensive. It appeared to support the usual interface fauna of fish, crustacea and other invertebrates possibly in reduced numbers, but these appeared to be absent in a central area where the deposit was continuous (as opposed to patchy in the fringe areas). Immediately by the outfall, there was a scoured area supporting active benthos surrounded by a fringe of wood chips. Many fish were present around the outfall, and epizootics on the pipe itself. There was no mill discharge during the period of the dives.

The surface of the white deposit was contoured into broad shallow depressions where patches of dark grey, apparently organic, floc gathered. In places there were holes in the deposit as though burrowing species were present or gas had bubbled through. Attempts to collect samples supported earlier observations that the deposit did not cohere well. Although the material could be lifted from the bottom by the submersible's mechanical arm, the material disaggregated on further movement, and no satisfactory samples were collected either directly by the arm's claws or by a mainipulated net.

Van Veen grab samples showed a reduced macrobenthos (2 mm screen used in sorting) with a species association to be expected in areas adjacent to pulp mill outfalls (Table 2). It contrasted clearly with the fauna of the reference area (Tables 3 and 4). A single trawl in the area of deposition was aborted due to irregular bottom. It produced no fish.

Prior to the field investigations, a literature search had been conducted reviewing seabed impact from pulp and paper mill discharges (Ellis and Ostrovsky, 1982) and their relevance to the Harmac situation. It was noted that although there was usually a benthic response of reduced fauna, the baseline species associations differed substantially from place to place, thus entailing considerable time and effort for effective documentation of lost biomass and habitat. The literature search also

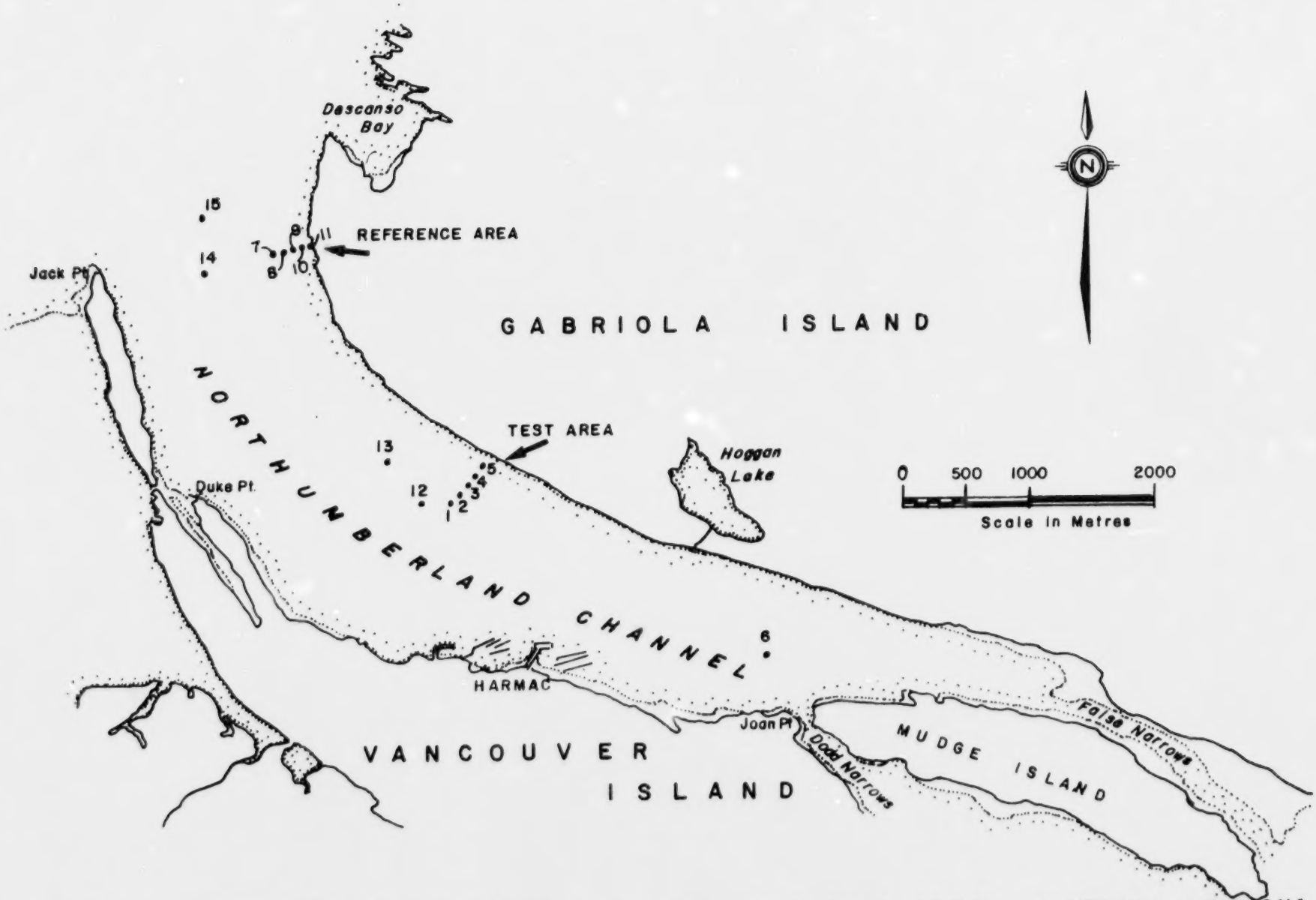


FIGURE 2 UNIVERSITY OF VICTORIA TEST AND REFERENCE AREAS - SAMPLING STATIONS FOR AUGUST 31 - SEPTEMBER 3, 1982 ARE SHOWN

TABLE 2 ORGANISMS IDENTIFIED FROM THE GRAB SAMPLES IN THE TEST AREA. SAMPLE POSITIONS SHOWN IN FIGURE 2.

| | GRABS | | | | | | |
|---|---|---|---|---|---|---|---|
| SPECIES | 1 | 2 | 3 | 4 | 5 | 12 | 13 |
| Depth in m | 115 | 110 | 105 | 100 | 95 | 103 | 108 |
| Capitella capitata | + | + | | + | + | | |
| Capitellidae (unidentified) | + | | | | | | |
| Antionella vittata | + | | | | | | |
| Solemya sp. | + | | | + | | | + |
| Echiurus echiurus alaskanus | + | | | | + | + | |
| Polychaeta (unidentified) | | + | | | | | |
| Heteromastus filiformis | | | + | + | | + | |
| Bivalvia (unidentified) sp. A | | | | + | + | | |
| Leptosynapta sp. | | | | | + | | + |
| Spiochaetopterus costarum (tubes) | | | | | | | + |
| No. spp. | 5 | 2 | 1 | 4 | 4 | 2 | 3 |

$\bar{m} = 3$

TABLE 3 ORGANISMS IDENTIFIED FROM THE GRAB SAMPLES IN THE REFERENCE AREA. SAMPLE POSITIONS SHOWN IN FIGURE 2.

| | GRABS | | | | | | |
|---|---|---|---|---|---|---|---|
| SPECIES | 7 | 8 | 9 | 10 | 11 | 14 | 15 |
| Depth in m | 115 | 110 | 105 | 100 | 95 | 103 | 108 |
| Goniada maculata | + | | | | | | |
| Nephtys punctata | + | | | | | | |
| Melinna cristata | + | + | + | | | | |
| Ampharita acutifrons | + | | | | | | |
| Polychaeta (unidentified) | + | | + | | + | + | |
| Bivalvia (juvenile) sp. 1 | + | + | | | + | + | |
| Gastropoda sp. 2 | + | | | | | | |
| Thyasira flexuosa | + | | | + | | | + |
| Leptosynapta sp. | + | + | + | + | + | + | + |
| Terebellides stroemi | | + | | | | | |
| Dentalium sp. | | + | | + | + | | |
| Goniada brunnea | | | + | | + | | + |
| Cylichna alba | | | + | | | + | |
| Heterophoxus oculatus | | | + | | | | |
| Onuphis irisdescens | | | | + | | | |
| Unidentified organism a | | | | + | + | | |
| Nephtys brachycephala | | | | | + | | |
| Phyllodoce castanea | | | | | + | | |
| Maldanidae | | | | | | + | |
| Unidentified organism b | | | | | | + | |
| Antionella vittata | | | | | | | + |
| Clycinde polygnatha | | | | | | | + |
| Spiochaetopterus costarum (tubes) | | | | | | | + |
| Gastropoda sp. 3 | | | | | | | + |
| Nuculana sp. | | | | | | | + |
| No. spp. | 10 | 5 | 6 | 5 | 8 | 6 | 8 |

$\bar{m} = 6.9$

TABLE 4 SUMMARY OF DIVERSITY AT THE TEST AND REFERENCE AREAS (SEE FIGURE 2)

| SPECIES | TEST | REFERENCE |
|---|---|---|
| Capitella capitata | + | |
| Solemya sp. | + | |
| Echiurus sp. | + | |
| Heteromastus filiformis | + | |
| Capitellidae | + | + |
| Antionella vittata | + | + |
| Bivalvia | + | + |
| Leptosynapta sp. | + | + |
| Spiochaetopterus costarum (tubes) | + | + |
| Polychaeta | + | + |
| Goniada maculata | | + |
| Goniada brunnea | | + |
| Nephtys punctata | | + |
| Nephtys ferruginea | | + |
| Melinna cristata | | + |
| Ampharita acutifrons | | + |
| Gastropoda | | + |
| Thyasira flexuosa | | + |
| Terebellides stroemi | | + |
| Dentalium sp. | | + |
| Cylichna alba | | + |
| Heterophoxus oculatus | | + |
| Onuphis irisdescens | | + |
| Phyllodoce castanea | | + |
| Maldanidae | | + |
| Glycinde polygnatha | | + |
| Nuculana sp. | | + |
| Unidentified organism | | + |
| $\bar{m}$ spp./station | 3 | 7 |

noted that in at least one marine area, Loch Eil in Scotland, receiving the discharge of a sulphite process mill, the seabed response of anaerobiosis had been investigated in some detail (Pearson, 1981; 1982). At Loch Eil a sulphuretum consisting of a variety of cellulose and sulphur metabolising bacteria had formed, and included the sulphide oxidising bacterium Beggiatoa. A detailed review of these widely distributed sulphur metabolising bacteria is provided by Postgate (1979) and Postgate and Kelly (1982).

The interface white deposit in Northumberland Channel was sampled by submersible, Craib corer and Van Veen grab during the 1982 surveys. Invariably the material dispersed and disappeared, but some of the core samples were taken for later examination. It was found that white filaments became visible after disturbed sediment settled down in samples held under refrigeration. On microscopic examination these were found to be large filaments tentatively identified as the Cyanobacterium Oscillatoria. Further literature search and microscopic examination later suggested that this was incorrect. The forms appear to be a large filament version of Beggiatoa. Both are to be expected (Fenchel and Riedl, 1970). There is some discussion among microbiologists and protophytologists about the phylogenetic relationships of Oscillatoria and Beggiatoa (Fenchel and Riedl, 1970; Postgate and Kelly, 1982). A variety of other bacteria may occur (Jorgenson, 1982). Attempts to culture the filaments using a number of mediums had some but limited success. Pure culture of these forms is difficult (C. Brown and L. Albright, personal communications).

The university field programme was reactivated in March 1983 with a second series of submersible dives. In these, submersible positions were plotted by means of buoyed line pulled tight over the stationary submersible by support boat at intervals, and position fixed by support ship's radar. It can be stated provisionaly that the mat distribution appears smaller than previously. Results are now being worked up.

Discussions with university colleagues who have made submersible and scuba diver observations elsewhere in southern B.C. indicate that similar white deposits occur in the low oxygen depths of Saanich Inlet (V. Tunnicliffe, personal communication), and near log storage areas (several graduate students).

## 3. SULPHURETUM INVESTIGATIONS AT LOCH EIL

The Loch Eil investigations, extending from 1963 to date during the time that a pulp and paper mill was operated by Scottish Pulp and Paper Mills Ltd., demonstrated usually benthic reduction accompanied by anaerobiosis in the pit of the Loch. Reviews by Pearson (1981, 1982) terminate and list a series of thirteen published primary research papers. The ecoysystem response is modelled in Figure 3. The investigators conclude that there is a net export of nutrients from the sulphuretum to the water column, that the extent of the sulphuretum is in equilibrium with the mill discharge (an average of 12 tonnes/day of suspended solids), and fluctuates over a period to be measured in weeks, with corresponding short-term fluctuations in bacterial density. There follow delayed responses in ciliate protozoan community (4 weeks), and the macrobenthic community (4-14 weeks). One of the contained bacteria is the aerobic sulphide oxidising form Beggiatoa.

## 4. CONCLUSIONS

The white deposit in Northumberland Channel is a bacterial mat of a type similar to that known to be formed by the aerobic sulphide metabolising Beggiatoa, and the ecosystem response to the Harmac discharge is provisionally modelled in Figure 4. Similar bacterial mats occur in many places in British Columbia coastal waters, at pulp mill discharges, at log storage and other areas, and are to be expected elsewhere. At Harmac the mat is a sulphide oxidising bacterial layer over the anaerobic

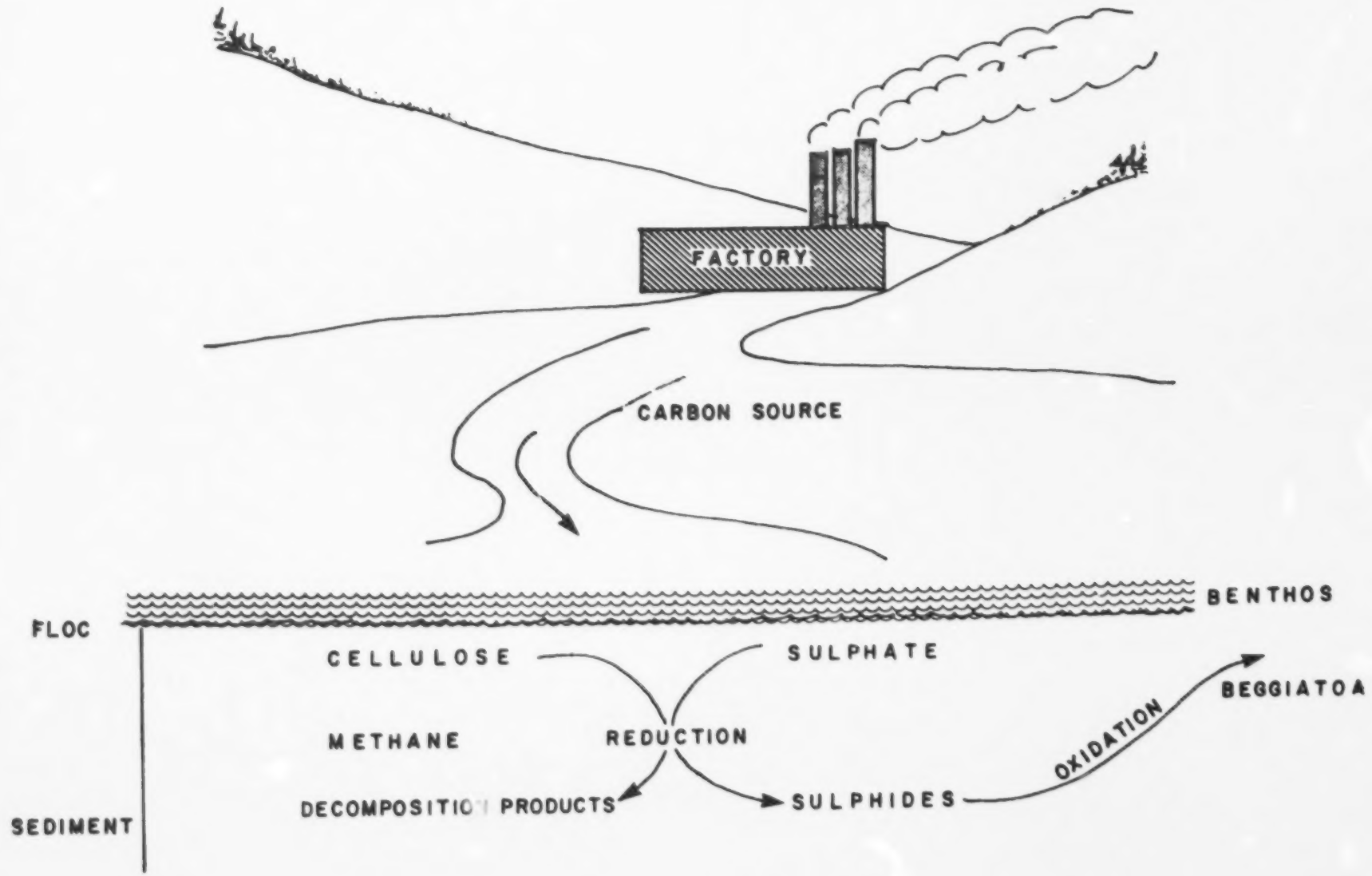


FIGURE 3 SIMPLIFIED MODEL OF THE LOCH EIL SULPHURETUM (Modified from Pearson, 1981)

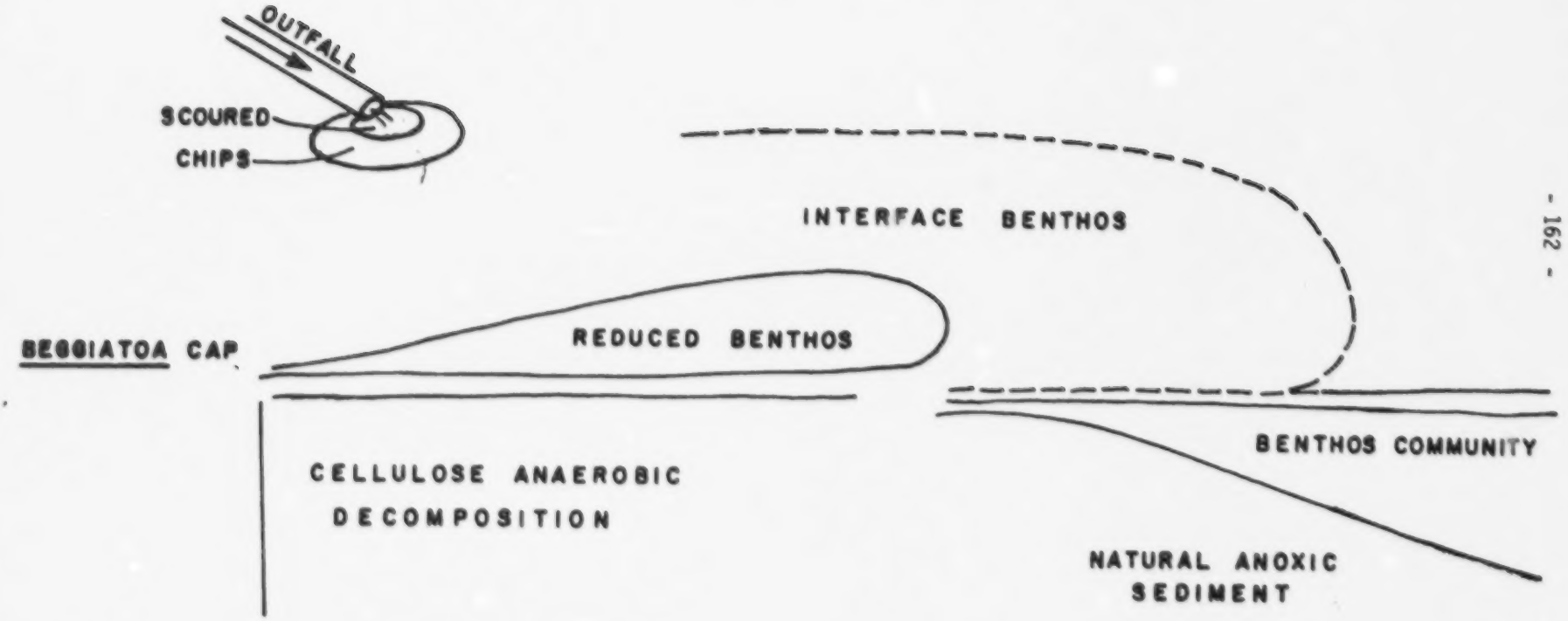


FIGURE 4 A MODEL OF A POSTULATED SULPHURETUM AT HARMAC

cellulose-decomposing (wood-fibre) component of the benthic system. The system appears to fluctuate in extend, may be in an equilibrium with carbon input (mill discharge) and not be expanding and accumulating indefinitely.

The aggregates trawled up by fishermen have not been seen during submersible surveys.

The present university investigation projected for 1982-84 is intended to demonstrate the nature of the macrobenthic response to the mill effluent and to identify at least some of the bacteria and environmental parameters involved. More detailed investigation of this ecosystem response to low oxygen/high carbon stress is needed if management actions are to be considered. The net nutrient recycling benefits of the system need quantifying compared to the cost of lost demersal fish habitat and feedstock biomass. Such an investigation should be made by a multidisciplinary team spearheaded by bacteriologists, with support from chemists and macrobenthic and fishery biologists at a number of naturally and mill induced sites.

The investigation could merit an unsolicited research proposal to the federal government by a multi-disciplinary team, but will need a "home" goverment agency providing appropriate support.

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# BIOCONVERSION OF PULP SLUDGE TO A PROTEIN BYPRODUCT

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## 1. INTRODUCTION

Envirocon holds the world-wide licence for a process capable of converting cellulose to protein. The process utilizes a fungal micro-organism which is encouraged to grow and consume cellulose. The microbial culture is harvested by filtration and drying and is a suitable substitute for soyameal in livestock feed formulations.

The pulp and paper industry processes many millions of tons of cellulose each year, however about one percent of this material finds its way into the mill effluent stream where it becomes a disposal problem. The statistics we have been able to check indicate that these losses amount to about one half million tons of cellulose per year in the U.S. Using our process, it would be possible to convert this cellulose to approximately 125,000 tons of crude protein. The protein market could readily absorb this quantity in that it represents less than two percent of the U.S. annual consumption of plant protein in animal feeds. On the other hand, however, it does represent a potential revenue of approximately $100 million per year.

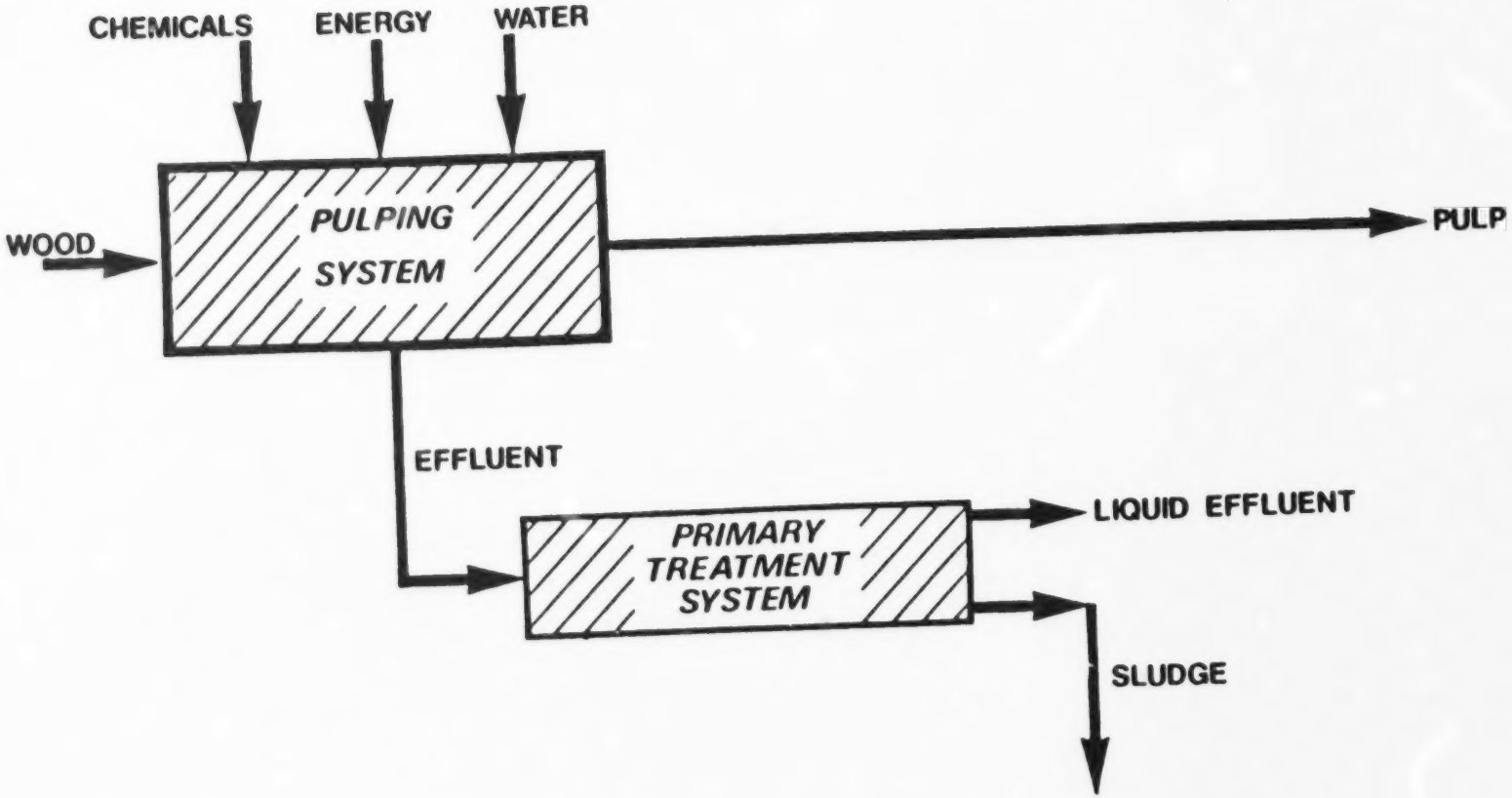
## 2. THE PROCESS

To put our activities over the last two years into persepctive, I should provide some historical background. Since the early '70's the process has been in the research phase at the University of Waterloo in eastern Canada. A laboratory scale pilot plant has been operated and waste cellulose from numerous sources has been tested. Samples of the protein product have been evaluated by conducting small scale feeding

trials on animals such as rats and rabbits. In 1980 Environcon purchased the licence for this process and with the aid of the Department of Industry, Trade and Commerce of the Canadian Government, we started design and construction of a large-scale pilot plant. This pilot plant is currently in its final stages of consutruction and we have started a program intended to evaluate and develop the process. If this evaluation confirms our original assessment, we will be in a position to market this process technology on a turn-key basis.

The process itself is quite simple. Figure 1 represents a very simplified block diagram of a chemical wood pulpling operation, note the waste sludge must be removed from the process and disposed of. The protein production process is designed to be integrated into this overall process as is shown in Figure 2. Sludge which had represented a disposal problem is now converted into a protein by-product. The process does use some low pressure steam and some nutrient chemicals as shown.

The block titled "Protein Production System" is displayed in more detail in Figure 3. The process consists of three distinct stages: pre-treatment, fermentation and product harvesting. Figure 4 is a flow diagram of the overall process which shows a yield of 7 tons of product for every 10 tons of sludge converted. This flow diagram is based on sludge having a cellulose content of 60%. Though the conversion takes place as a result of a biological growth process, it can be represented by the equation shown at the bottom of this figure. Note that only half of the cellulose is converted tc protein or biomass and the remainder forms carbon dioxide and water. This explains the 30% weight loss between the feedstock and the product. It is important to note that the microbe consumes only cellulose and as a result the non-cellulosic ash component passes through unaffected. Also the wood component remains unconverted as well, because its cellulose is protected by the lignin. Kraft mill sludge is an ideal substrte or feedstock because it contains a significant portion of delignified cellulose. Although in theory the only pre-treatment required for kraft sludge is sterilization to eliminate any


CHEMICALS
ENERGY
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WOOD
PULPING SYSTEM
PULP
EFFLUENT
PRIMARY TREATMENT SYSTEM
LIQUID EFFLUENT
SLUDGE

FIGURE 1

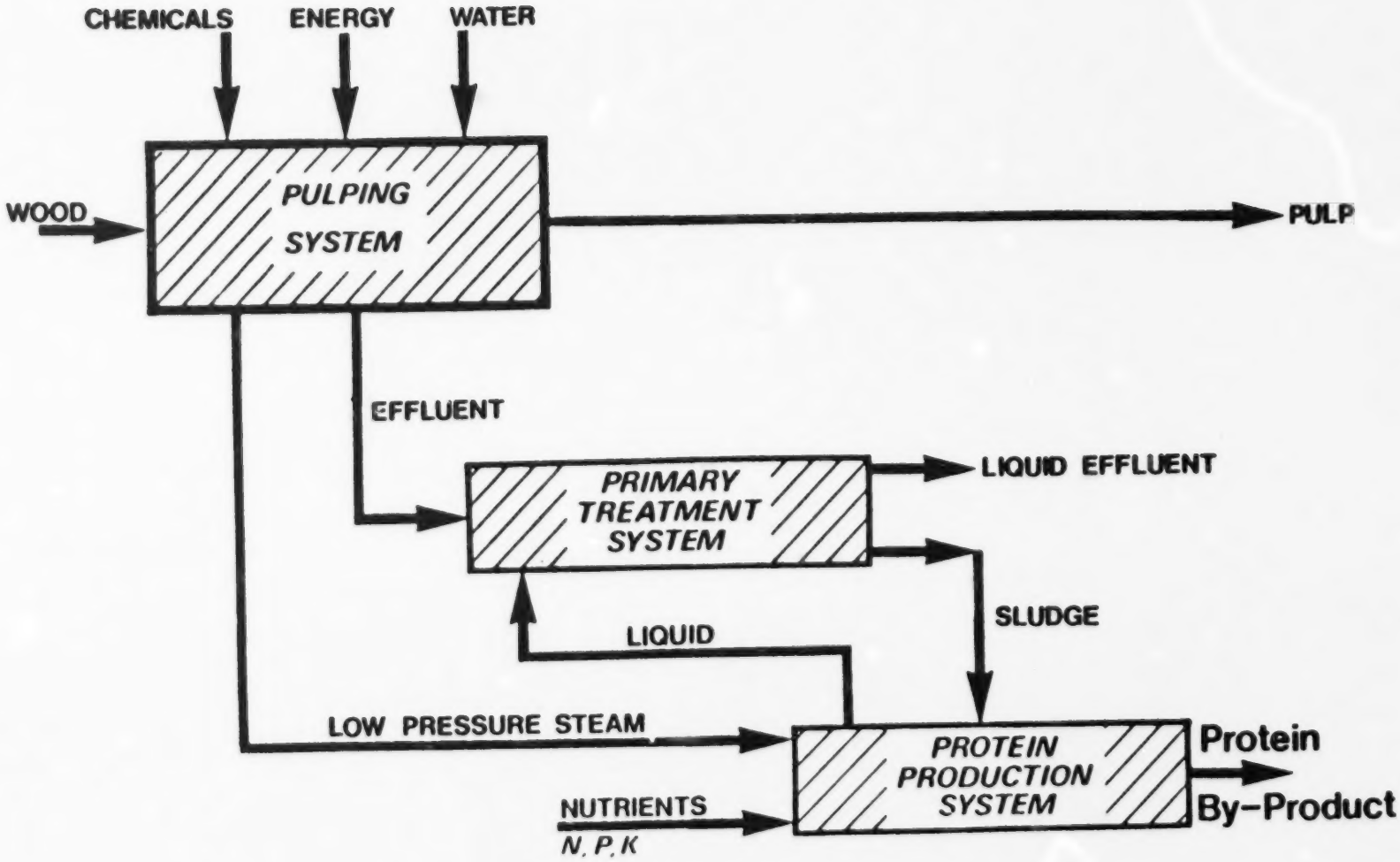

CHEMICALS
ENERGY
WATER
WOOD
PULPING SYSTEM
PULP
EFFLUENT
PRIMARY TREATMENT SYSTEM
LIQUID EFFLUENT
SLUDGE
LIQUID
LOW PRESSURE STEAM
PROTEIN PRODUCTION SYSTEM
Protein
By-Product
NUTRIENTS
N, P, K

FIGURE 2

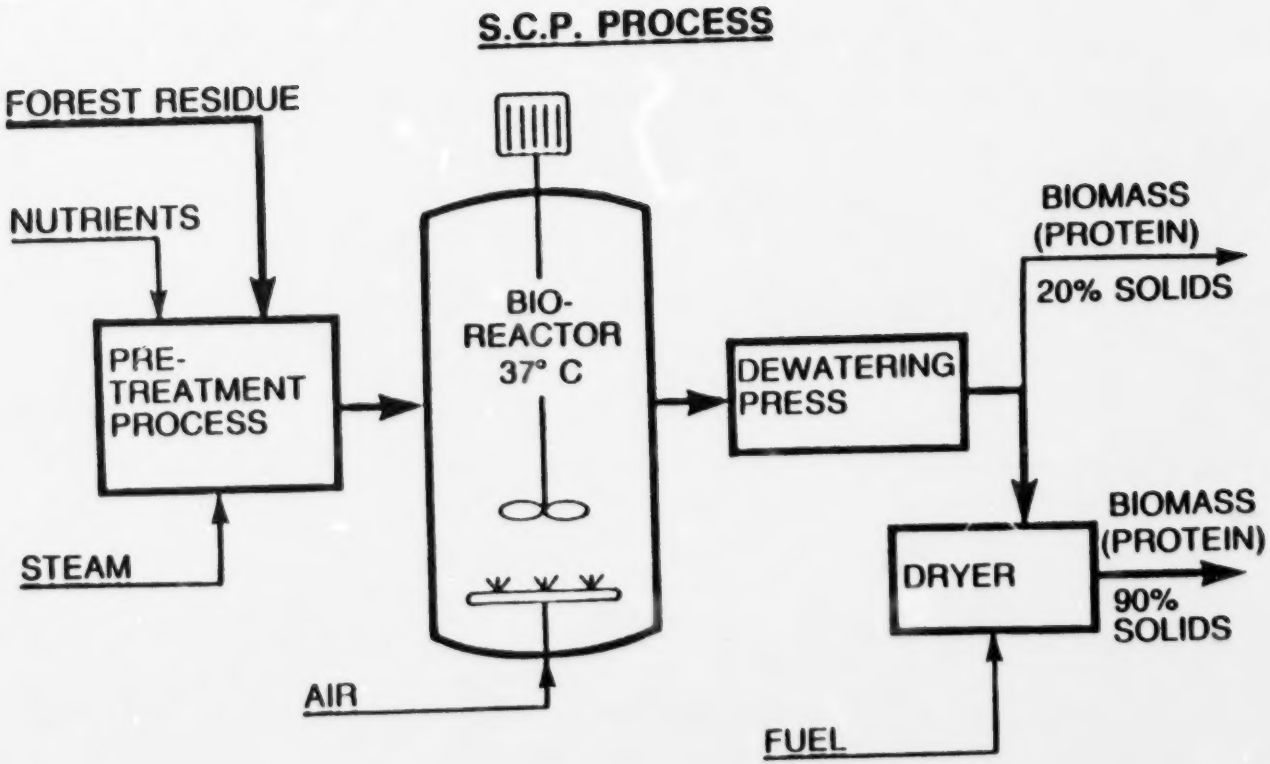

S.C.P. PROCESS
FOREST RESIDUE
NUTRIENTS
PRE-
TREATMENT
PROCESS
STEAM
BIO-
REACTOR
37° C
AIR
DEWATERING
PRESS
BIOMASS
(PROTEIN)
20% SOLIDS
DRYER
BIOMASS
(PROTEIN)
90%
SOLIDS
FUEL

FIGURE 3

# TYPICAL UNCONDITIONED KRAFT MILL SLUDGE

| SLUDGE | | REJECTS | PRODUCT | | | 100% BASIS |
|---|---|---|---|---|---|---|
| CELLULOSE | 60% | → | BIOMASS → PROTEIN | 15% | | 21% |
| | | | → CARBOHYD. FATS, etc | 15% | | 21% |
| WOOD (INCLUDING LIGNIN) | 30% | → | | 30% | | 43% |
| ASH | 10% | → | | 10% | | 15% |
| TOTAL SOLIDS | 100% | 0% | TOTAL | 70% | | 100% |

$$10(CH_2O)_n + 5O_2 + NH_3 \rightleftharpoons 5CH_aO_bN_c + 5CO_2 + 5H_2O$$

CELLULOSE — BIOMASS

FIGURE 4

competitors for the fungus, in practice the unfermentable components of kraft sludge have a significant dilution effect on the final product. Though cattle can digest a certain amount of ligno-cellulose, poultry and swine receive no benefit from it whatsoever. To reduce this dilution effect, it is appropriate to screen out the bulk of the wood and ash. Figure 5 shows about 3/4 of this non-fermentable material being separated as part of the pre-treatment. Note that this has improved the protein content from 21% to 40% which will nearly double the value of the product.

The heart of the process is the fermentation stage. It is in this stage that the fungus called Chaetomium cellulolyticum is encouraged to feed on the cellulose. This stage of the process takes place in the fermenter which is a cylindrical vessel equipped to provide aeration and agitation of the substrate slurry. The pH is controlled at approximately 6 and the average residence time in the fermenter is 8.5 hrs. The operating conditions for the fermenter are listed in Figure 6.

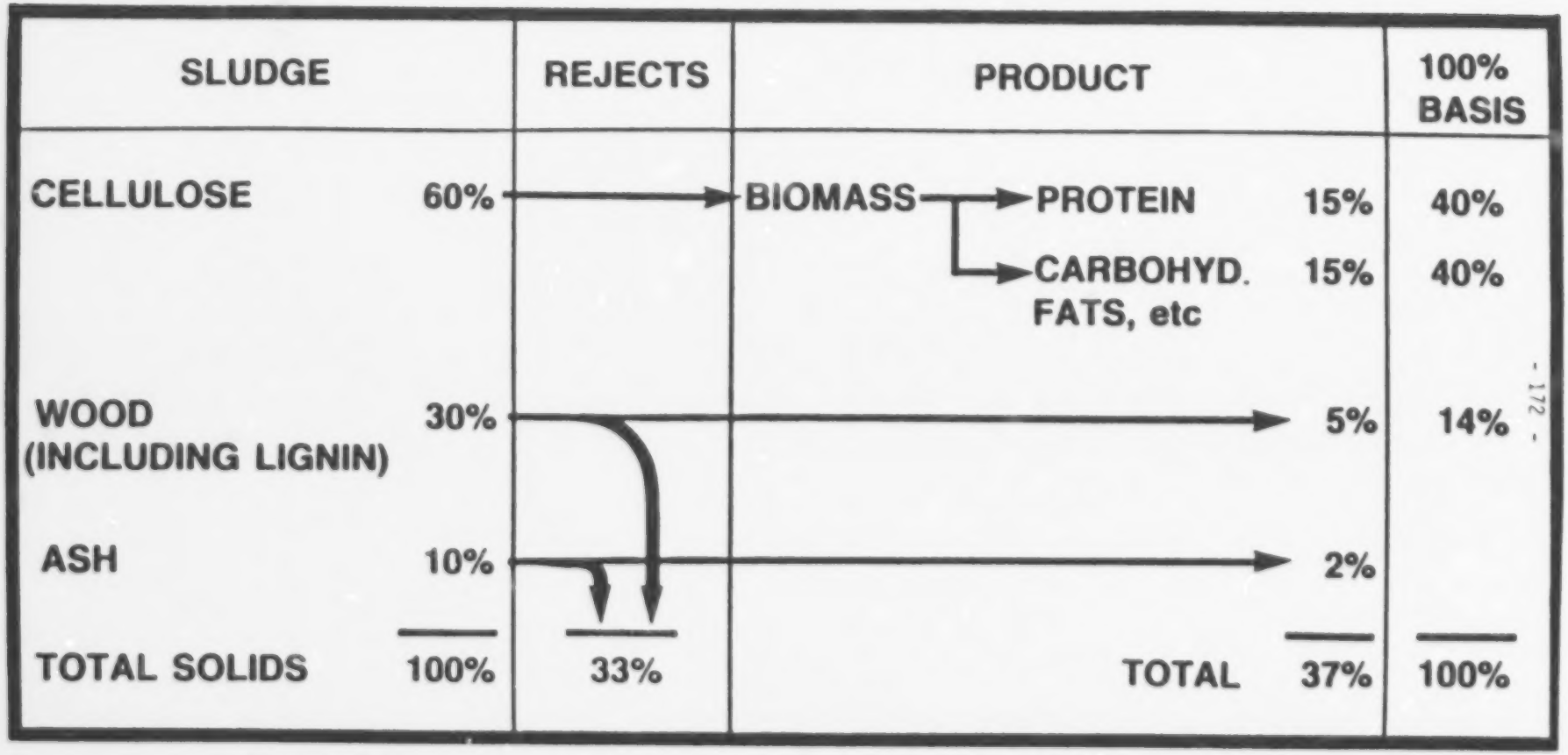
Following fermentation, the free liquid is separated by a mechanical device such as a vacuum drum filter, centrifuge or belt press. This operation raises the product's solids content to about 20%. In certain operating situations it may be possible to feed directly to livestock in this condition however it is more likely that the product will require drying to about 90% solids. The dry product would have shelf life in excess of a year.

## 3. PILOT PLANT CONSTRUCTION

As was mentioned earlier, Envirocon is nearing completion of a pilot plant in Vancouver. Originally our intention was to arrange for a pulp mill to host the pilot plant but this was not possible. As an alternative we have assembled the equipment in structural steel modules which have been installed in the yard of Forintek Canada Corporation, a private organization specializing in forest products research. If it is

FIGURE 5

# TYPICAL CONDITIONED KRAFT MILL SLUDGE




$$10(CH_2O)_n + 5O_2 + NH_3 \rightleftharpoons 5CH_aO_bN_c + 5CO_2 + 5H_2O$$

CELLULOSE — BIOMASS

## TYPICAL OPERATING CONDITIONS FOR AEROBIC FERMENTATION OF PRIMARY CLARIFIER SLUDGE USING *CHAETOMIUM CELLULOLYTICUM*

| | |
|---|---|
| STERILIZATION TEMPERATURE, °C | 121 |
| OPERATING TEMPERATURE, °C | 37 |
| CELLULOSE CONCENTRATION IN FEED, % OF DRY SOLIDS | 65 |
| SOLIDS CONCENTRATION IN FEED, % OF TOTAL FEED | 3 |
| UTILIZATION OF CELLULOSE, % | 90 |
| YEILD OF S.C.P. CELL PRODUCTION/CELLULOSE UTILIZED | 0.5 |
| AIR REQUIREMENT, VVM | 0.2 |
| CARBON/NITROGEN RATIO IN FEED | 8/1 |
| N/P/K RATIO IN FEED | 20/2/1 |
| PROTEIN CONTENT OF PRODUCT | 30 |

FIGURE 6

warranted by the results from our evaluation, we will be able to move the pilot plant module to waste cellulose sources for production trials at a later date.

## 4. PILOT PLANT OPERATION

Though construction is not yet complete, we have producecd some protein in the pilot plant. Our work program calls for a series of runs on pulp sludge to gather the necessary engineering data to design a full-scale plant. Also we expect to optimize the operation of this process on the pilot scale and to collect the information necessary for a detailed study of its economic performance. An important part of this economic study is the suitability of the product as an animal feed. This is determined by conducting feeding trials with the target species of animals. To date the quantities of product available have not permitted the feeding trials on commercial animals such as poultry, swine and cattle, however our pilot plant has sufficient capacity to provide product for these trials.

The feeding trial results that we have are quite encouraging. Figure 7 summarizing the results of trials on rabbits indicates that there was no problem with palatibility and that the weight gain per unit of feed was nearly identical to the control. The control ration was composed of conventional feed ingredients with the protein source being soyameal. Figure 8 shows similar results for trials conducted on rats.

## 5. CONCLUSION

To summarize, Environcon is evaluating and hoping to commercialize a process capable of converting kraft mill sludge into a protein by-product for use in livestock feeds. The process involves pre-treatment of the sludge, fermentation by a fungus, and harvesting

# FEED TRIALS conducted by J.G. Buchanan – Smith published April 30, 1981

**GROWTH, FOOD INTAKE AND FEED EFFICIENCY OF RABBITS FED CONTROL AND SCP DIETS FROM CHAETOMIUM GROWN ON WOOD PULP SLUDGE[a]**

| | FEED INTAKE g/DAY | AVERAGE DAILY GAIN, g | FEED/GAIN |
|---|---|---|---|
| CONTROL | 108.04 ± 27.6 | 26.75 ± 5.63 | 4.04 ± .47 |
| SCP-24, 15% | 115.25 ± 30.2 | 25.75 ± 8.45 | 4.58 ± .52 |

[a] 5 RABBITS PER TREATMENT, MEAN ± SD

FIGURE 7

# FEED TRIALS conducted by J.G. Buchanan – Smith published April 30, 1981

**GROWTH, FOOD INTAKE AND FEED EFFICIENCY OF RATS FED CONTROL AND SCP DIETS FROM CHAETOMIUM GROWN ON WOOD PULP SLUDGE**

| TRIAL 2[b] | FEED INTAKE g/DAY | AVERAGE DAILY GAIN, g | FEED/GAIN |
|---|---|---|---|
| CONTROL | 25.30 ± 1.96 | 6.78 ± 1.03 | 3.81 ± .67 |
| SCP-PP24, 15% | 27.10 ± 1.89* | 6.78 ± 1.04 | 4.07 ± .52 |
| SCP-PP24, 30% | 26.44 ± 1.65 | 5.73 ± .71* | 4.68 ± .68* |

[b] 12 RATS PER TREATMENT, MEAN ± SD

* SCP DIFFERENT FROM CONTROL, $P < 0.05$

FIGURE 8

using conventional equipment. Preliminary economic evaluations indicate the product will cost between $200 nd $250 per ton to produce and that it is very similar to soyameal in its performance as a feed ingredient.

# A CONCEPTUAL APPROACH TO PULPMILL POLLUTION RESEARCH

Lee Harding
Environmental Protection Service
Environment Canada
Kapilano 100, Park Royal
West Vancouver, B.C.
V7T 1A2

## 1. INTRODUCTION

There are users and producers of knowledge. Users - agencies, institutions and people within them - apply knowledge to some practical problem. In control of pulpmill effluents, users are environmental regulatory agencies and company officials who decide what technology is appropriate and necessary based on the knowledge of the potential and real effects the effluent will have on environmental resources; and who decide whether or not to purchase, install, modify, prosecute and so on.

Producers are the scientists and technologists, the practitioners of applied and basic research that produces new knowledge on physical, chemical and biological processes. The purpose of this seminar is to bring the producers of knowledge together with the users, to review the status of existing knowledge relative to pulpmills, and to identify knowledge gaps to be filled during the 1980's. The purpose of my talk is to discuss the kinds of information which are needed to make pollution control decisions. I propose to raise three or four topics and put questions to participants, by way of stimulating discussion.

## 2. KINDS OF KNOWLEDGE

Knowledge is produced in a heirarchical system (Figure 1):

### 2.1 Biological

- cellular

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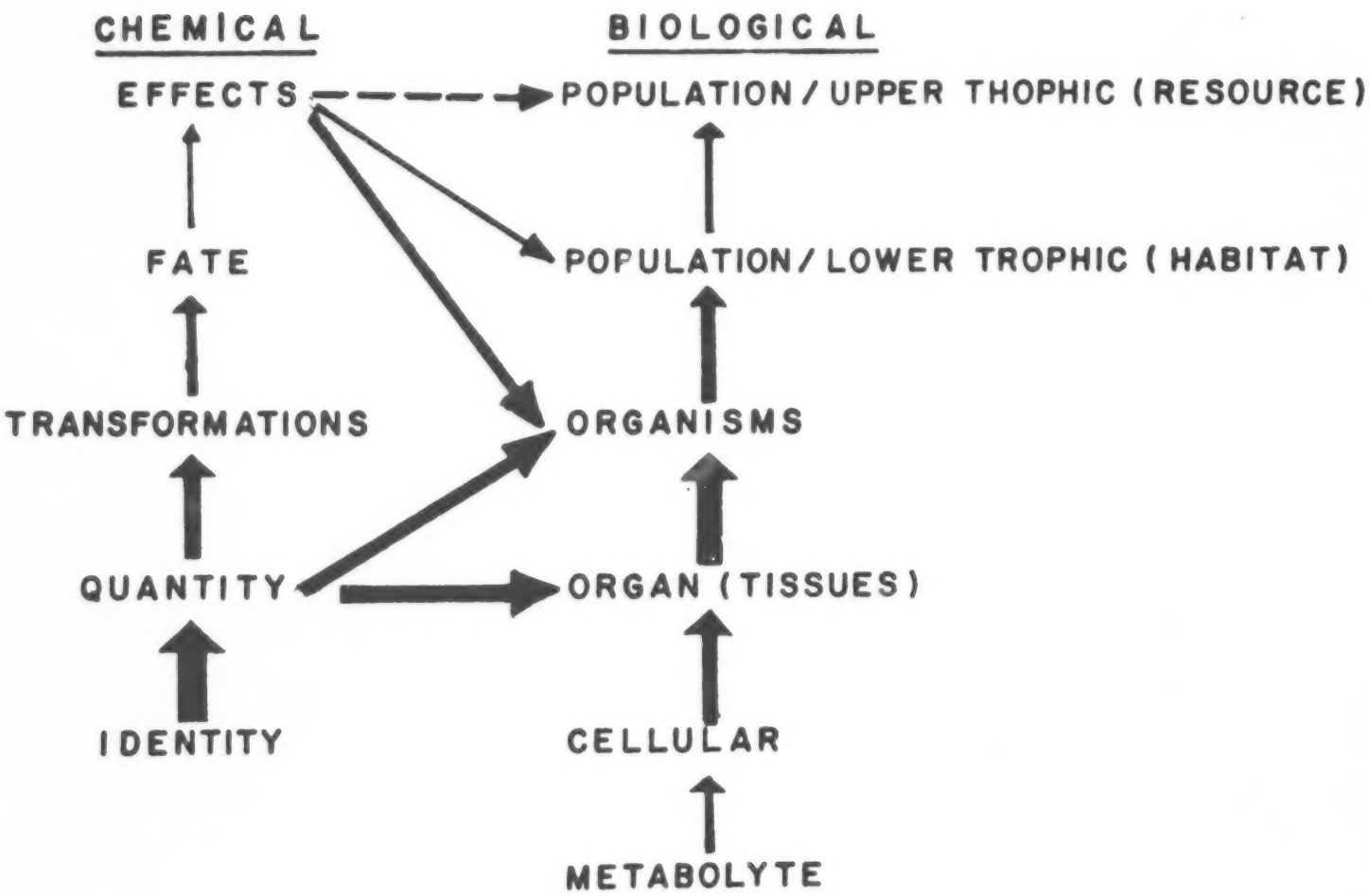


FIGURE 1 HIERARCHICAL SYSTEMS OF KNOWLEDGE PRODUCTION IN TWO AREAS: BIOLOGICAL AND CHEMICAL ENVIRONMENTAL STUDIES. VECTORS INDICATE COMMON DIRECTIONS OF INTEGRATION IN RELATION TO POLLUTION RESEARCH

- organ function accumulation in tissues, detoxification sequesting, excretion metabolism
- organism (toxicity, tainting)
- population of lower trophic levels (habitat)
- population of commercially or recreationally important resources

2.2 Chemical

- identification
- quantitation
- description of transformations
- description of transportation
- determination of fate

I called these hierarchical, rather than sequential, because each level depends on, rather than merely following, the one below it. The information needed to decide on pollution control measures is at the top of the figure.

The ultimate question is: How will the discharge (or proposed changes) affect the resource that is used by man?

Question: Can anyone suggest a case in British Columbia for discussion where pollution is presently reducing commercial fish stocks?

Corollary: How many such situations are known? Of all habitat being lost, how much is due to pollution?

The conclusion is (probably) that the link between the lower levels of investigation and the higher levels is rarely drawn. Why not?

## 3. CURRENT PROGRAMS

In 1976 the Fisheries Research Board of Canada reviewed the problems of aquatic environmental quality in Canada[1] and concluded that an excessive amount of pollution monitoring data was being collected

in relation to the level of interpretation. They further concluded that an excessive amount of point source monitoring effort was being expended in relation to the amount of non-point source monitoring effort. In 1982, Dr. D. Ellis reviewed the status of marine environmental monitoring in British Columbia and concluded essentially the same thing: that there was insufficient monitoring of ambient conditions, and that existing monitoring data are poorly integrated.[2] Let us examine current pollution monitoring programs to determine if the necessary knowledge is being produced to make pollution control decisions:

The Environmental Protection Service marine monitoring program is a hierarchical process of source and receiving water information development:

3.1 Source

3.1.1 Level 1.

a) All liquid discharges to the marine environment in British Columbia are required to have a provincial permit. Federal agencies are consulted to ensure federal requirements are included as conditions. Both provincial and federal agencies maintain a computer inventory of discharges, updated continually. Permit applications and permits contain soft (predicted) or hard (measured) data on effluent quality.

b) All solid discharges to the marine environment are required to have a federal permit. Applications include hard data on material particularly toxic chemicals of concern to environmental or human health values. Data are computer-achieved to allow evaluation of spatial and temporal trends.

3.1.2 Level 2. Companies, municipalities and individuals with significant (in the opinion of administering agencies) discharges in 1(a) above are required to monitor and report their effluent quality to provincial agencies. These data are routinely referred to federal agencies. In addition, some industrial sectors under federal regulation are required to report directly to federal authorities. Complexity ranges from annual or more frequent measurement of parameters of interest (such as toxic chemicals, toxicity or biochemical oxygen demand) to a thorough mass balance for the element(s) of concern (eg., mercury at chlor-alkali plants).

3.1.3 Level 3. Federal and provincial agencies measure effluent quality regularly for certain marine discharges and on an "as needed" or "as time permits" for others. In addition, both levels of goverment investigate non-permitted discharges.

3.2 Receiving Environment

3.2.1 Level 1. Application for discharges come with at least a map, from which some receiving water information can be obtained or guessed. Depending on circumstances considerable additional data may accompany the application.

3.2.2 Level 2. Pollutors are required to monitor conditions in the receiving environment of each company for parameters liable to change and of importance to harvestable resources. Reporting is to the provincial agencies (and referred to Federal agencies) and, for federally regulated operations, directly to federal agencies.

3.2.3 Level 3.

a) Environmental Protection Service attempts to monitor or audit receiving water conditions at all significant sources of continuous marine

pollution in British Columbia, "significant" being in this case those with the potential to effect human health or harvestable resources. Parameters selected to identify links at appropriate trophic levels between (but not including) pollutant sources and resources at risk, may include dissolved oxygen, toxic chemicals (sediments and biota), benthic community assemblages, water quality and primary productivity ($C_{14}$ or Chlorophyll a). Extent is sufficient to define the zone of impact. Frequency is related to rate of change of environmental parameters and changes in effluent quality/waste handling: most sites are sampled multi-annually some annually or biannually. Programs are designed to compliment, supplement or audit (confirm validity of) company programs. Included in the program are:

- all coastal pulpmills
- all mines
- all cities and some smaller towns experiencing change in effluent treatment
- all commercial shellfish harvesting areas
- all Ocean Dump Sites.

b) Provincial agencies have similar, less comprehensive marine monitoring programs, usually coordinated with federal programs.

c) Resource management agencies (eg., CWS, DFO, B.C. Marine Resources) monitor resources at some levels such as breeding populations and harvest size.

d) Application for new developments or modification of existing development are often accompanied by consultant reports supplemented by government surveys on the receiving environment, and these provide data additional to routine programs, especially in embayed ares of multiple discharges. For example, B.C. Hydro (Sasamat Plant) and Pacific Coast

Terminals have completed, at the agencies' request, environmental surveys in their respective receiving environments and these collectively supplement other monitoring and research data on Port Moody arm, an embayed, multiple discharge area.

3.2.4 Level 4. Federal and provincial agencies, universities and industrial associations (eg., COFI) investigate specific pollution phenomena ranging in scope and complexity from brief site inspections to multi-year research.

The foregoing describes both the kind and amount of our point source monitoring. I will not deal further with amount, since it is dictated by budgetary resources, except to reiterate and support conclusions of FRB and Ellis that non-point source effort lags far behind point source monitoring.

Regarding the kind of monitoring, you can see that it deals primarily with organ, organism and lower trophic levels (refer to Figure 1). Basic and applied research also provides information on these levels, as well as the lowest, or cellular levels, and on the influences of chemical and physical processes on these levels. Finally, resource managers know something about the population of resources at the top of the diagram, those of interest to man.

Question: How well are these kinds of knowledge integrated, generated as they are by different agencies with different mandates in a way that will assist pollution control decisions?

Are there suggestions for improvement?

## 4. KNOWLEDGE NEEDED TO SUPPORT POLLUTION CONTROL DECISION

Pollution control decision-making is not a heirarchical system, but rather a dichotomous one (Figure 2). Note that the information needed is the impact on resources of interest to man, real or probable. The fact

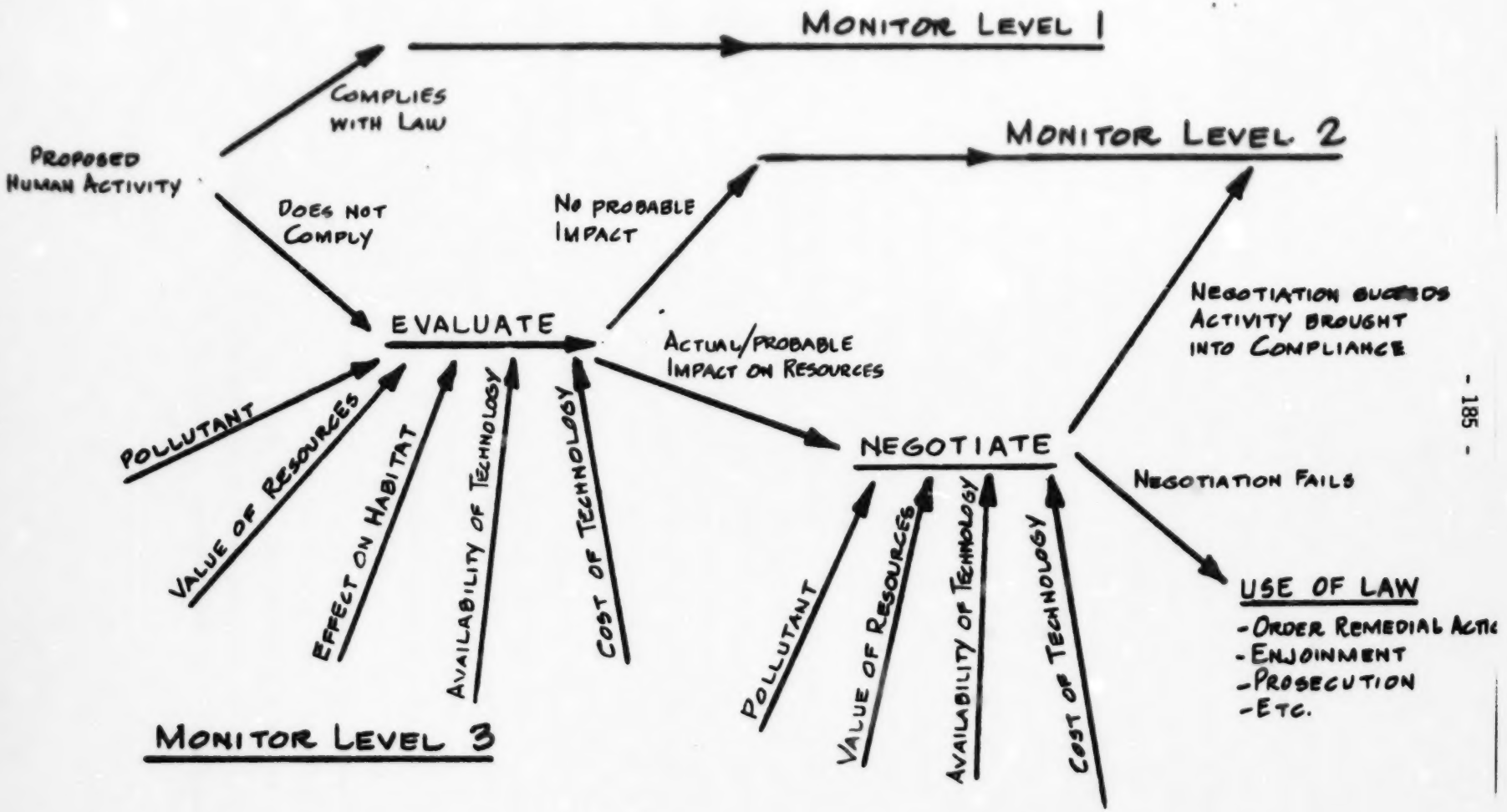


FIGURE 2 POLLUTION CONTROL DECISION PROCESS FOR RESOLUTION OF RESOURCE USE CONFLICTS

that some process or effect exists and can be measured at the cellular, organ or organism level, by itself is not sufficient to base a pollution control decision where some cost to society is involved. For example, the fact that bioaccumulation occurs and can be measured as a result of some pollutant is not sufficient information on which to base a pollution control decision. Bioaccumulation by itself is not necessarily harmful to man's interest. It only becomes a hazard it if occurs to the extent of reducing diversity or abundance of species, or rendering inedible a population of man's food fishery, or degrading the fishes habitat; or of biomagnifying in the food chain to the point where it affects man's food fishes or himself.[3] Marine food webs are typically unstructured, with diffuse energy flow; the lack of structure and undirectional flow that are characteristic of classical food chain models may prevent the amplification of pollutants at higher levels.[4] Pollutants acumulate and are easiest measured in sediments, and pollution monitoring and research programs most frequently focus on benthic processes and populations. In Figure 3, a very simple arctic food web, note that loss of any one or several benthic groups would not necessarily threaten higher levels, since they have alternative food sources. Similarly, the potential for biomagnification is slight. Carried to its epitome the knowledge base would be sufficient to answer the question, what level of pollution abatement will result in a measureable increase in production of harvestable resources? In this way, the resources would not be wasted by making "improvements" with no benefit to society.

Unfortunately, in my perception, many pollution control decisions are made without knowledge of an actual or probable impact at the population level of a resource to man. This is because most environmental monitoring and scientific research effort is expended on the lower levels of investigation. I have heard it said that a sensible policy, in the absence of such knowledge, is to err on the conservative side, that is, to base the decision on knowledge of a process or phenomenon which has some theoretic, potential effect of unknown

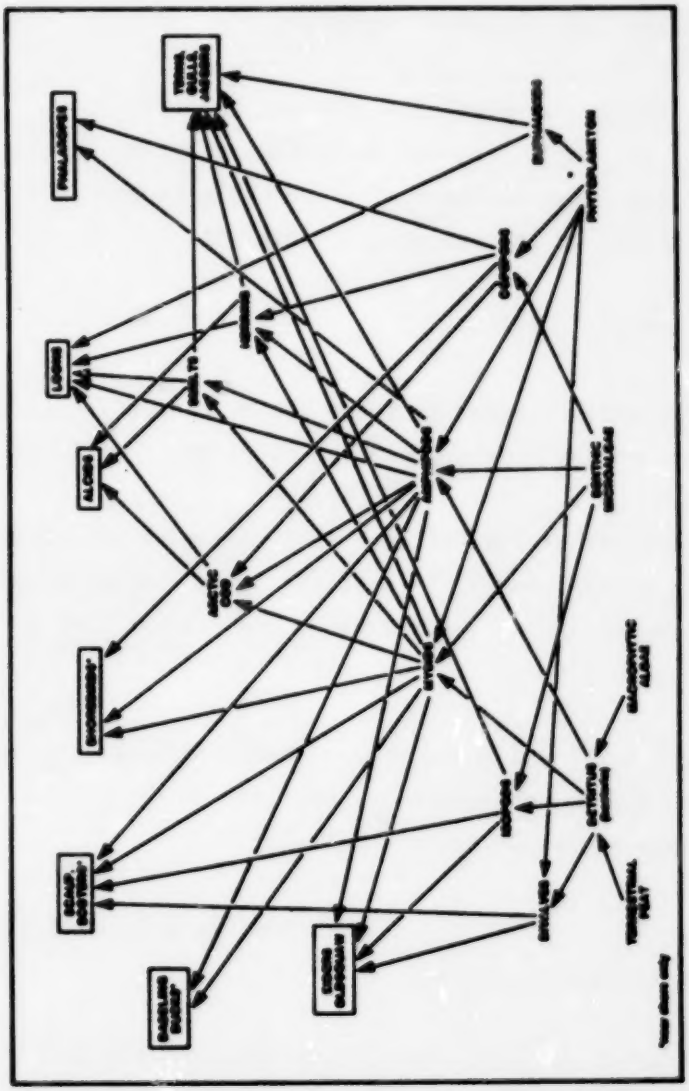

Figure 3 Artic Food Web

(from Hydrocarbon Development in the Beaufort Sea - Mackenzie Delta Region. Volume 3A)

probability; and indeed this is often the basis for pollution control decisions. But an error is an error, whether conservative or liberal. Our goal is to make perfect decisions. This is not merely an ideal: it is a moral, ethical and legal imperative.

Question: How can we eliminate the need to err?
Conclusion: By conducting our research and our monitoring programs to bridge the gap between potential or possible impacts and actual or probable impacts on the resource of interest.

## 5. SUGGESTED PRIORITIES

Recently I asked my three senior biologists to suggest a list of research priorities. Those relating to pulpmill effluent include:

1. Toxic effects of various levels of contaminants, as measured in tissues of the commercial species; aside - most toxicity is on dissolved pollutants in sea water, but we can't measure them in sea water routinely;

2. Further studies of toxic effects and avoidance reactions of migrating fish to various pollutants as measured *in situ*, such as those described yesterday by Eric McGreer;

3. Biomagnification of inorganic contaminants through successive trophic levels in marine food webs;

4. Behaviour of pulpmill effluent on entering the marine environment: flocculation, chemical alteration etc.;

5. Availability of contaminants sequestered in sediments: mobility, chemical interactions, bio-uptake and lethal and sublethal toxicity;

6. Recolonization rate and type (eg., alteration of community structure) following perturbation by wood fiber/deposition;

7. Natural and pollution-induced variation in incidence of pathological conditions in commercial species, in relation to persistent compounds in pulpmill effluents;

8. Trophic relationships of commercial species, to species affected by pulpmill effluents, (eg., prey species of sole at various age classes and alternative feeding strategies, such as was done at Alberni Harbour with salmon);

9. Variations in fish population and productivity in response to point and non-point source pollution, compared to natural variations.

Question: Further suggestions?

## 6. REFERENCES

1. Fisheries Research Board of Canada Interim Report on Aquatic Environmental Quality in Canada, Ottawa, February, 1976.

2. Ellis, D.V. Ocean Disposal in British Columbia. Proceedings, Oceans' 82 Marine Pollution Papers, pp. 1101-1106.

3. Harding L. Use of Fjords for Disposalfo Mine Tailing, Preprint of Proceeding, Coastal Zone '83, San Diego, California, June 1-4, 1983.

4. Isaacs, J.D. Assessment of Man's Impact on Marine Biological Resources in Marine Pollution and Marine Waste Disposal, E. Pearson and E. de Ia Fraja Frangipane, Eds., (Elmstord, N.Y.: Pergamon Press), pp. 320-340.

POOR

QUALITY

ORIGINAL